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THE SPINNING AND FLOATING OF LIGHT BODIES IN AN ELECTRIC FIELD: DEVELOPMENT OF AN EXPERIMENT OF SIR ISAAC NEWTON

By LORD RAYLEIGH, F.R.S.

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WHILE preparing an address on " Newton as an Experimenter " for the recent tercentenary celebration, * a paper by him in an early volume of the *Philosophical Transactions* was consulted. This is apparently the very earliest communication received by the Royal Society on any electrical subject, and would not seem at first sight a likely source of inspiration for anything of novelty today. However, an effect is there described which was new to me, and seemed to call for further investigation.

> *From the Minutes of the Royal Society.* 9 *December* 1675.
>
> That [Newton] having laid upon a table a round piece of glass about two inches broad, in a brass ring, so that the glass might be about one-third of an inch from the table, and the air between them inclosed upon all sides after the manner as if he had whelved a little sieve upon the table: and then rubbing the glass briskly, till some little fragments of paper, laid on the table under the glass, began to be attracted and move nimbly to and fro; after he had done rubbing the glass, the papers would continue a pretty while in various motions; sometimes leaping up to the glass and resting there awhile; then leaping down and resting there, and then leaping up and down again; and this sometimes in lines perpendicular to the table sometimes in oblique ones; sometimes also leaping up in one arch and down in another divers times together, without sensible resting between; sometimes skip in a bow from one part of the glass to another, without touching the table; and sometimes hang by a corner and turn often about very nimbly, as if they had been carried about in the midst of a whirlwind; and he otherwise variously moved every paper with a diverse motion. And upon sliding his finger on the upper side of the glass, though neither the glass nor inclosed air below were moved thereby, yet would the papers, as they hung under the glass receive some new motion inclining this or that way, according as he moved his finger.
>
> The experiment he proposes to be varied with a larger glass placed farther from the table, and to make use of bits of leaf gold instead of papers, esteeming that this will succeed much better, so as perhaps to make the gold rise and fall in spiral lines or whirl for a time in the air, without touching the table or glass.
>
> Ordered that this experiment be tried the next meeting.

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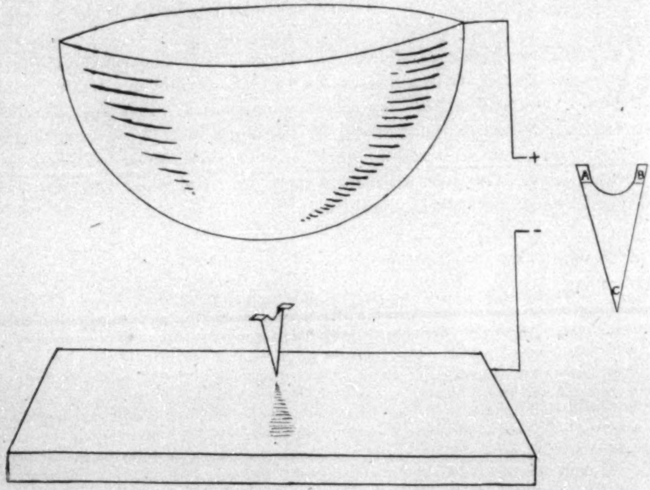
* *Proc. Roy. Soc.* A, **181**, 244–250 (1943).

The earlier part of these observations are not altogether forgotten,* but I have not found anything further about the spinning effect described by Newton, either in Priestley's *History of Electricity* (1767) or in more modern books. In arranging to repeat the experiments for the centenary celebration above mentioned, I noticed this spinning of some of the pith fragments, though this was an exceptional effect, only shown by a few of them, and not to be relied on or reproduced with certainty. It was attempted, therefore, to develop the experiment into a more definite and dependable form, if possible on a larger scale.

In order to do this, electrified insulators as used by Newton were avoided, metal conductors at a definite potential being used instead. Further, the light body was made of aluminium foil instead of pith. With this material the shape could more easily be controlled and specified.



Passing over some intermediate steps, I will describe the experiment in its final shape.

A Whimshurst machine is used as the source of electrification. It is connected to a strip of brightly reflecting tinplate as the base, and to a copper hemisphere (from a ball cock) 13 cm. in diameter, which is supported on insulating pillars, 4 cm. minimum distance from the base plate. For easy commutation, lead weights are connected to the wires from the machine. One of these lies inside the copper hemisphere, the other on the base plate. They can readily be exchanged. This is preferable to more elaborate commutators, which offered too many opportunities for loss by brush discharge and defective insulation.

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* When I was a small boy, Sir William Thomson, afterwards Lord Kelvin, came on a visit to my parents, possibly about the year 1886, and brought with him, as a present for my brother and myself, a fascinating toy embodying an elaborated form of this experiment. It consisted of a flat tray, measuring perhaps 12 × 12 × 1½ inches, covered with tin foil, with a glazed top, probably flint glass. The tray contained jointed pith figures. These danced vigorously when the glass was rubbed with a soft leather pad. On enquiring from Messrs. Hamley, I could not learn that any such toy had been on sale in recent years.

The spinning piece is of aluminium foil, 0 05 mm. in thickness. The shape and size are as shown in the inset, but it is to be understood that the lugs at A and B, as shown in the inset, are bent out of the plane of the paper, A being above the paper, B below.

This piece lies on the base plate. When the machine is started, the upper electrode (hemisphere) being positive, the aluminium piece gets up on end, the bigger end, AB, above, and spins about the pointed end C. C rests on the base plate and acts at first as a pivot.

The direction of rotation is that due to recoil from an electric wind blowing away from the points A and B. On working the machine faster so as to increase the potential to an equivalent spark gap of 5 mm. corresponding to, say, 15,000 volts, the spinner rises away from the base plate, as may be readily verified by noticing that the bottom end C no longer coincides with its image seen by reflection in the bright tin plate, but is separated by a definite interval, which may even increase to several millimetres. The aluminium spinner is then touching nothing, and we have in this experiment one solution of the problem of "Mahomet's coffin", i.e. the support of a solid body without contact with anything material except the air.* It fully realizes the possibility, tentatively mentioned in the above quotation from Newton, which, so far as appears, he did not definitely achieve himself.

If the experiment is performed in the dark, luminous discharges may be seen at the top points AB and the bottom point C of the spinner.

The hemispherical bowl as the upper electrode secures that the electric field should be stronger in the middle than further out, and prevents much lateral wandering of the spinner.

The experiment does not work satisfactorily unless the upper electrode (copper hemisphere) is made positive and the base plate negative. The Whimshurst may start with either polarity, and it is necessary to verify it, for which a small vacuum discharge tube is convenient. With wrong polarity the aluminium spinner floats higher, but is much less stable, and does not spin with anything like the same definiteness.

The pointed end of the spinner sometimes tends to stick to the base plate, rotating in contact with it. A tap on the base plate (with a wooden ruler, e.g.) will detach it and cause it to rise. It then continues to spin without touching the base plate. As a demonstration it can well be projected on the screen.

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* The well known experiment of supporting a light ball on a jet of air is, of course, a better solution. The aeroplane is another.

AN EMISSION BAND-SYSTEM OF PbSe

By R. F. BARROW and E. E. VAGO,
Physical Chemistry Laboratory, Oxford

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ABSTRACT. A band-system (D→X) assigned to PbSe has been excited by a heavy-current, uncondensed, positive-column discharge through the vapour of PbSe contained in a silica tube. About 40 bands in the region 3350–3850 A. have been photographed in the first order of a grating instrument with dispersion ~7·4 A./mm. The vibrational analysis leads to the following expression for the wave-numbers of the band-heads :

$$\nu_{\text{head}}=28416\cdot9+(190\cdot5u'-0\cdot6u'^2)-(277\cdot4u''-0\cdot56u''^2),$$

where $u=v+\frac{1}{2}$. The identity of the value of ω_e'' with that for the ground state of PbSe, obtained by Walker, Straley and Smith, 1938 (*Phys. Rev.* **53**, 140) from analyses of absorption systems, shows that the lower state of the new transition is the ground state.

§ 1. INTRODUCTION

The work described in this and in the following paper is part of a programme which, it is hoped, will throw some light on the sequence and correlation of excited electronic levels in the oxides, sulphides, selenides and tellurides of tin and lead. For no molecule in this group are the existing data entirely satisfactory. Adequate vibrational analyses have been made of at least one strong band-system of each molecule, but the present schemes for weaker and sometimes overlapping systems are, in many cases, unconvincing. Earlier work on SnSe (Barrow and Vago, 1943) showed that study of the emission spectra might usefully supplement information obtained from absorption experiments. The present paper describes a band-system of PbSe obtained in emission.

§ 2. EXPERIMENTAL

The source used was a heavy-current, uncondensed, positive-column discharge (~2000 V., ~2 A.) through the vapour of PbSe contained in a silica tube. The experimental arrangements have been described before (Barrow, 1941). Photographs were taken in the first order of a 2·4-m. grating (dispersion ~7·4 A./mm.) on Ilford Ordinary plates.

The principal feature in the spectrum is a system of about 40 red-degraded bands in the region 3350–3850 A., shown in the accompanying plate. The wave-lengths of the band-heads were measured against Fe arc standards (*M.I.T.*, 1939): these are included in the Deslandres scheme, given in the table. The wave-numbers of the band-heads are represented satisfactorily by the equation

$$\nu_{\text{head}} = 28416\cdot9+(190\cdot5u'-0\cdot6u'^2)-(277\cdot4u''-0\cdot56u''^2),$$

where $u=v+\frac{1}{2}$.

PbSe D→X system : Band-head data

Italic numerals denote wave-lengths in air (I.A.) ;
Large Roman, wave-numbers *in vacuo* (cm.$^{-1}$) ;
Small Roman, wave-number differences.

* Measure uncertain on account of 1, 0 band ;
† Head obscured by Pb λ 3639·580 ;
‡ Head obscured by Pb λ 3739·947 ;
§ Head obscured by Pb λ 3683·471.

v' ↑ / v'' →	0		1		2		3		4		5		6		7		8		9
9			29763·0 *3358·92*	278·1	29484·9 *3390·6*														
			176·7																
8			29586·3 *3378·98*																
			187·2																
7	29677·2 *3368·62*	278·1	29399·1 *3400·49*																
			185·2																
6			29213·9 *3422·05*																
			185·0																
5	29307·5 *3411·12*	278·6	29028·9 *3443·86*																
	186·3		185·5																
4	29121·2 *3432·95*	277·8	28843·4 *3466·01*	272·5	28570·9* *3499·06*														
	184·0		183·4		186·0														
3	28937·2 *3454·78*	277·2	28660·0 *3488·19*	275·1	28384·9 *3521·99*														26497 *3772·9*
	185·7		184·6		183·1														188
2	28751·5 *3477·09*	276·1	28475·4 *3510·80*	273·6	28201·8 *3544·86*	275·2	27926·6 *3579·80*	275·0	27651·6 *3615·40*	269·9	27381·7 *3651·04*		§				26576·5 *3761·66*	268	26309 *3800·0*
	188·2		187·8		189·2		187·5				187·2						191·2		192
1	28563·3 *3500·00*	275·7	28287·6 *3534·11*	275·0	28012·6 *3568·81*	273·5	27739·1 *3604·00*	275·0	†		27194·5 *3676·17*	272·6	26921·9 *3713·39*	268·3	26653·6 *3750·77*	268·3	26385·3 *3788·92*	268	26117 *3827·8*
	188·9		188·7		189·9		189·7				189·7				186·0		184·4		
0	28374·4 *3523·30*	275·5	28098·9 *3557·85*	276·2	27822·7 *3593·16*	273·3	27549·4 *3628·81*	272·0	27277·4 *3665·0*	272·6	27004·8 *3701·99*		‡		26467·6 *3777·14*	266·7	26200·9 *3815·59*		

Detailed interpretation of the rather complicated isotope effect for this molecule was not possible with the dispersion used, but the effect provides qualitative confirmation of the assignments in so far as the sharpest heads are those nearest to the postulated system-origin.

§ 3. CONCLUSION

The spectrum of PbSe has also been studied in absorption by Walker, Straley and Smith (1938). These authors assigned some 180 bands to three systems (upper states A, B, C) lying to the red of the present system. Their expression for the ground-state vibrational terms based on the analysis of the three systems is $G''(v'')=277\cdot78u''-0\cdot452u''^2$. This is so close to the result given by the present analysis, i.e., $G''(v'')=277\cdot4u''-0\cdot56u''^2$, that there can be little doubt that the lower state of the new transition is also the ground state. The system is therefore designated (D→X).

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THE ABSORPTION SPECTRUM OF SnTe

By R. F. BARROW and E. E. VAGO,
Physical Chemistry Laboratory, Oxford

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ABSTRACT. The absorption of SnTe vapour in the visible region of the spectrum has been studied in the temperature range 800–1400° C. in evacuated silica tubes. About 140 bands have been measured on plates taken in the first order of a 2·4-m. grating (dispersion ~7·4 A./mm.). These have been assigned to four systems, one of which (D⇌X, $\nu_e\sim25450$ cm.$^{-1}$) has already been observed in emission by Barrow, 1940 (*Proc. Phys. Soc.* **52,** 380). The data for this molecule are summarized below :

State	ν_e	ω_e	$x_e\omega_e$
E	~27500	—	—
D	25444·3	179·1	0·40
C	21418·6	218·1	0·98
B	20394·9	239·3	1·53*
A	16844·0	178·5	0·44
X	0	259·5	0·50

* $y_e\omega_e=-0\cdot013$.

§ 1. INTRODUCTION

One fairly well developed system of bands assigned to SnTe appears in emission in positive-column discharges through the mixed vapours of Sn and Te (Barrow, 1940). By analogy with the similar molecules SnSe (Walker, Straley and Smith, 1938; Barrow and Vago, 1943) and PbSe

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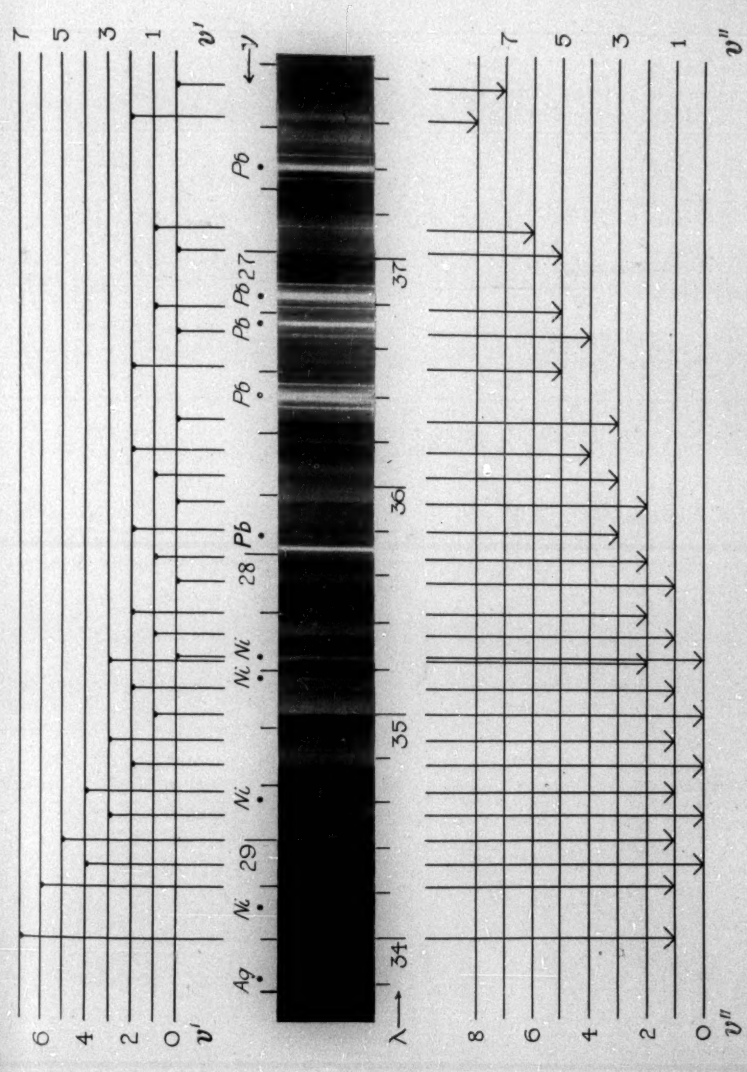

Bands of the D→X system of PbSe in emission (2·4-m. grating, first order).

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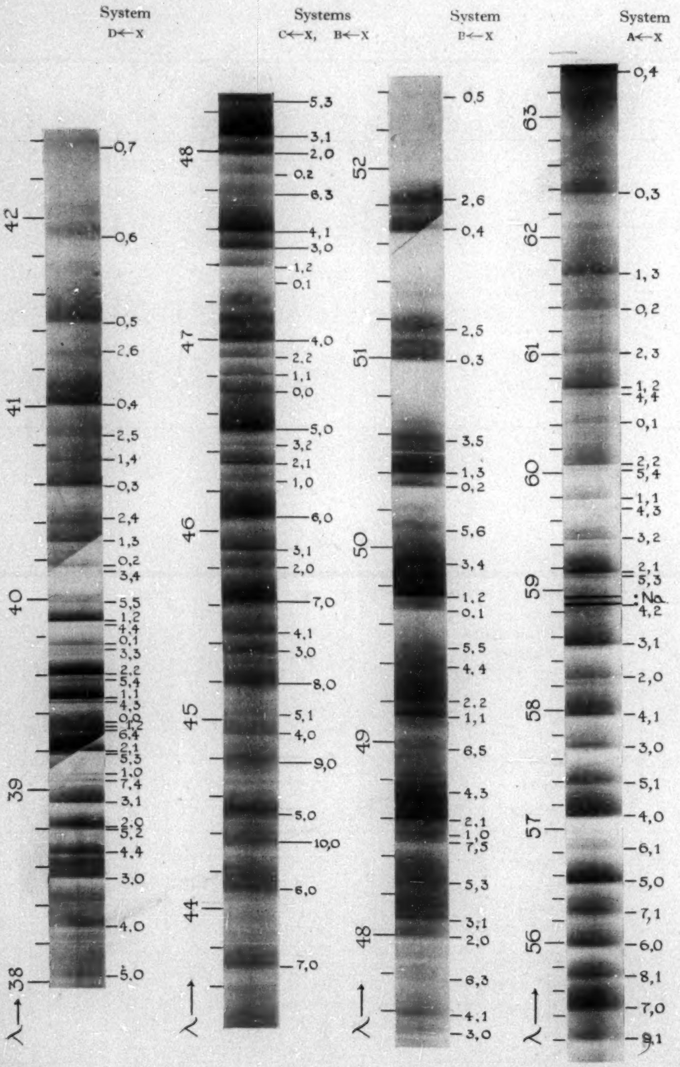

The absorption spectrum of SnTe (2·4-m. grating, first order).

(Barrow and Vago, 1944), other systems of SnTe lying to the red of the emission system were expected to appear in absorption. Bands belonging to three such absorption systems have now been photographed and analysed, and new data have been obtained on the system which also appears in emission.

§ 2. EXPERIMENTAL

The experimental arrangements were simple. SnTe was prepared by heating together rather less than the stoicheiometric proportion of Te with Sn. 5 to 10-g. charges of the powdered material were placed in a silica boat inside a vitreosil combustion tube (length 55 cm., internal diameter 3 cm.), wound over the central third of its length with "Red Fox 135" resistance wire and lagged with fireclay and asbestos. Water-cooled glass adaptors carrying quartz windows were waxed on to each end of the tube; to one of these was sealed a tap leading to a pump used for preliminary evacuation. The source of continuum was a 500-w. tungsten-filament projection lamp. Spectrograms were taken in the first order of a 2·4-m. grating (dispersion ~7·4 A./mm.) on Ilford Ordinary and Special Rapid Panchromatic plates. Exposure times were 1–30 minutes. Absolute intensities among the systems seemed to decrease steadily in the direction of decreasing electronic energy, so that satisfactory contrast on the heads of the system of longest wave-length (A←X) was only obtained at the higher pressures where the absorption at shorter wave-lengths due to the other three systems appeared to be continuous. Reproductions of the spectrograms are given in the accompanying plate, and the band-head data are summarized in the Deslandres scheme set out in tables 1–4.

§ 3. RESULTS

System A←X

About 35 bands in the range 5300–6400 A. were assigned to this system. The vibrational analysis (table 1), which presented no difficulties, is qualitatively confirmed by the isotope effect, discussed in detail in another paper (Barrow, 1940).

Systems B←X, C←X

Some 40 bands in the region 4475–5300 A. and 20 bands between 4300 and 4800 A. were assigned to systems B←X and C←X respectively. The clue to the analyses of these overlapping systems (tables 2 and 3) was provided by the vibrational isotope effect. It was not possible with the dispersion used to recognize band-heads of individual isotopic species, but qualitatively the two regions of maximum sharpness of band-heads at about 4900 A. and 4675 A. (see plate) were of considerable value—not only in confirming the opinion that the bands in this region belong to two systems, but also in locating roughly the positions of the two system-origins. The system B←X is well developed, but for C←X the weaker bands with $v''>2$ are not observed, doubtless because they are to be expected in a region covered by the strong absorption of the B←X system.

System D⇄X

In the first account of this system of SnTe as obtained in emission (Barrow, 1940), it was designated *A→X*. The new lettering has been adopted to

Table 1. SnTe system A←X: Band-head data

Italic numerals denote wave-lengths in air (I.A.);
Large Roman, wave-numbers *in vacuo* (cm.$^{-1}$);
Small Roman, wave-number differences.

v′	v″→0		1		2		3		4		5
12			18621·1 *5368·77*								
			171·0								
11			18450·1 *5418·52*								
			168·7								
10			18281·4 *5468·52*								
			170·2								
9			18111·2 *5519·92*								
			170·0								
8			17941·2 *5572·23*								
			172·7								
7	18027·6 *5545·50*	259·1	17768·5 *5626·39*								
	171·5		172·7								
6	17856·1 *5598·76*	260·3	17595·8 *5681·59*								
	173·5		172·2								
5	17682·6 *5653·72*	259·0	17423·6 *5737·74*				16910·4 *5911·88*	255·2	16655·2 *6002·47*		
	174·5		174·4				177·0		174·2		
4	17508 1 *5710·07*	258·9	17249·2 *5795·77*	258·8	16990·4 *5884·06*	257·0	16733·4 *5974·42*	252·4	16481·0 *6065·93*	253·7	16227·3 *6160·75*
	176·4		173·9		173·2						
3	17331·7 *5768·17*	256·4	17075·3 *5854·80*	258·1	16817·2 *5944·66*						
	175·8		176·8		175·4						
2	17155·9 *5827·30*	257·4	16898·5 *5916·04*	256·7	16641·8 *6007·31*	256·3	16385·5 *6101·29*				
			176·7		176·2		176·2				
1			16721·8 *5978·57*	256·3	16465·6 *6071·59*	256·3	16209·3 *6167·60*	255·3	15954·0 *6266·28*	250·2	15703·8 *6366·1*
			176·8		177·6		178·3		178·2		
0			16545·0 *6042·44*	257·0	16288·0 *6137·79*	257·0	16031·0 *6236·18*	255·2	15775·8 *6337·07*		

Table 2. SnTe system B←X : Band-head data

Italic numerals denote wave-lengths in air (I.A.) ;
Large Roman, wave-numbers *in vacuo* (cm.$^{-1}$) ;
Small Roman, wave-number differences.

* ? also the 0, 3 of system C←X.

v' ↑ / v''→	0		1		2		3		4		5		6
9	22325 *4478·0*												
	205												
8	22119·5 *4519·64*												
	208·4												
7	21911·1 *4562·62*										20629·7* *4846·04*		
	211·8										211·8		
6	21699·3 *4607·15*						20927·8 *4777·00*		—		20417·9 *4896·31*		
	213·5						211·7				212·3		
5	21485·8 *4652·94*						20716·1 *4825·82*	257·7	20458·4 *4886·62*	252·8	20205·6 *4947·77*	252·3	19953·3 *5010·31*
	212·5						216·6		214·6				
4	21273·3 *4699·42*	260·9	21012·4 *4757·77*		—		20499·5 *4876·80*	255·7	20243·8 *4938·40*		—		
	219·9		218·1				218·1		219·6				
3	21053·4 *4748·51*	259·1	20794·3 *4807·68*	257·4	20536·9 *4867·92*	255·5	20281·4 *4929·25*	257·2	20024·2 *4992·56*	254·9	19769·3 *5056·94*		
	219·6		220·4		220·6		222·8				219·7		
2	20833·8 *4798·55*	259·9	20573·9 *4859·17*	257·6	20316·3 *4920·78*	257·7	20058·6 *4984·01*				19549·6 *5113·77*	254·7	19294·9 *5181·27*
	225·5		224·8		224·0		223·0						
1	20608·3 *4851·06*	259·2	20349·1 *4912·85*	256·8	20092·3 *4975·64*	256·7	19835·6 *5040·04*	255·7	19579·9 *5105·87*		—		
			227·8		228·8		228·0		226·8				
0	—		20121·3 *4968·48*	257·8	19863·5 *5032·96*	255·9	19607·6 *5098·64*	254·5	19353·1 *5165·70*	255·4	19097·7 *5234·78*	254·0	18843·7 *5305·33*

Table 3. SnTe system C←X: Band-head data

Italic numerals denote wave-lengths in air (I.A.);
Large Roman, wave-numbers *in vacuo* (cm.$^{-1}$);
Small Roman, wave-number differences.

9	23272·5 *4295·71*				
	200·5				
8	23072·0 *4333·04*				
	200·3				
7	22871·7 *4371·00*				
	204·9				
6	22666·8 *4410·50*				
	206·8				
5	22460·0 *4451·11*	258·2	22201·8 *4502·89*		
	209·7		211·1		
4	22250·3 *4493·07*	259·6	21990·7 *4546·10*		
	209·6		208·3		
3	22040·7 *4535·79*	258·3	21782·4 *4589·59*	257·3	21525·1 *4644·44*
	212·6		212·2		213·3
2	21828·1 *4579·98*	257·9	21570·2 *4634·74*	258·3	21311·9 *4690·92*
	215·1		215·9		215·3
1	21613·0 *4625·56*	258·7	21354·3 *4681·59*	257·7	21096·6 *4738·79*
	214·7		215·7		214·4
0 ↑ v'	21398·3 *4671·96*	259·7	21138·6 *4729·36*	256·4	20882·2 *4787·43*
	v''→0		1		2

Table 4. SnTe system D⇆X : Band-head data

Wave-lengths, I.A., are given in italics.

Wave-numbers, cm.⁻¹: **bold-face** denotes bands measured both in absorption and in emission;
large Roman, bands measured in absorption only;
large Roman,* bands measured in emission only.

Wave-number differences, cm.⁻¹, are given in small Roman numerals.

v′ ↑	v″→0		1		2		3		4		5		6		7
8	26809·6* *3728·95*	256·6	26553·0* *3764·98*												
	172·6		177·4												
7	26637·0* *3753·12*	261·4	26375·6* *3790·31*						25604·2 *3904·50*						
	167·8								172·0						
6	26459·2* *3778·34*		—						25432·2 *3930·89*	254·6	25177·6 *3970·66*				
	170·3								172·2		173·8				
5	26288·9 *3802·81*	258·5	26030·4* *3840·57*	255·7	25774·7 *3878·68*	259·6	25515·1 *3918·15*	255·1	25260·0 *3957·71*	256·2	25003·8 *3998·27*				
	172·4		176·1				175·3		175·8						
4	**26116·5** *3827·92*	262·2	**25854·3** *3866·73*		—		25339·8 *3945·25*	255·6	25084·2 *3985·45*						
	176·5		176·3				174·5		175·3						
3	**25940·0** *3853·96*	262·0	**25678·0** *3893·28*	257·1	25420·9 *3932·66*	255·6	**25165·3** *3972·59*	256·4	**24908·9** *4013·52*						
	179·8		176·3		176·8				178·1						
2	**25760·2** *3880·86*	258·5	**25501·7** *3920·20*	257·6	25244·1 *3960·19*		—		24730·8 *4042·40*	260·3	**24470·5** *4085·39*	255	**24215** *4128·5*		
	178·7		177·3		177·5				178·9		175·8		173		
1	25581·5 *3907·97*	257·1	**25324·4** *3947·64*	257·8	**25066·6** *3988·25*	257·4	**24809·2** *4029·63*	257·3	**24551·9** *4071·86*	257·2	24294·7 *4114·96*	253	24042 *4158·2*	257	**23785** *4203·[illegible]*
	177·1		179·4		178·6		178·7		176·4		172·2		177		178
0	25404·4 *3935·22*	259·4	**25145·0** *3975·82*	257·0	**24888·0** *4016·86*	257·5	**24630·5** *4058·86*	255·0	**24375·5** *4101·33*	253·0	24122·5 *4144·33*	257	**23865** *4189·0*	258	**23607** *42*

conform with empirical classification already used for systems of similar molecules (e.g. SnS, SnSe, PbSe).[*] Comparison of the plates of this system as developed in emission and in absorption showed that in the range 3800–4250 A. the latter were more complete.[†] In fact the new measurements have nearly doubled the number of assigned bands. Particularly useful in confirming the analysis and in increasing the accuracy of the vibrational constants is the relatively strong development in absorption of bands of the 1,0 and 0,0 sequences, which extend as far as the 6,5 and 5,5 bands respectively. These bands provide good values for the higher $\Delta G''$ and $\Delta G'$ differences—values which are probably more accurate than those obtained from the lower v' and v'' progressions, where certain identification of the head due to the most abundant isotopic species becomes increasingly difficult with increasing distance of these bands from the system-origin. The data given in table 4 therefore summarize both sets of measurements.

The weighted means of differences from all four systems were used in calculating the values of the ground-state vibrational terms. The expression obtained was $G''(v'') = 259 \cdot 5u'' - 0 \cdot 50u''^2$. This differs somewhat from that originally put forward from the analysis of the $\mathrm{D} \rightleftharpoons \mathrm{X}$ system in emission, i.e. $263 \cdot 7u'' - 1 \cdot 1u''^2$, but the new values, representing more extensive observations, are to be preferred. It is also to be noted that the new value of $x_e''\omega_e''$ is in line with the general trend observed for other molecules of this group, thus:

Table 5. Values of $x_e''\omega_e''$

	O	S	Se	Te
Ge	4·30	1·80	1·2	1·0
Sn	3·73	1·34	0·88	0·50
Pb	3·70	1·20	0·45	0·12

Finally, the derived values of ν_e and of the upper-state vibrational constants are given in table 6. The relations of these data to those of similar molecules in this group will be discussed in a later paper.

Table 6. Constants for electronic states of SnTe

State	ν_e	ω_e	$x_e\omega_e$
E	27500	—	—
D	25444·3	179·1	0·40
C	21418·6	218·1	0·98
B	20394·9	230·3	1·53*
A	16844·0	178·5	0·44
X	0	259·5	0·50

* $y_e\omega_e = -0 \cdot 013$.

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[*] Similarly the fragment, also obtained in emission, of what may be another system of SnTe involving the ground state, which was previously called $B \rightarrow X$ (Barrow, 1940), is now called I → . Recent absorption spectrograms (January 1944) have confirmed the existence of this system $\mathrm{E} \rightleftharpoons \mathrm{X}$. [Note added 2 February 1944.]

[†] For practical reasons, the low-λ limit of the present absorption measurements was about 3800 A.

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THE BAND SPECTRUM OF N_2: WEAK SYSTEMS IN THE VISIBLE REGION

By A. G. GAYDON, D.Sc.,
Chemical Engineering Department, Imperial College, London S.W.7

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ABSTRACT. The spectrum of N_2 produced by mild excitation with a silent, ozonizer-type discharge, and with a Tesla coil has been studied. The Goldstein-Kaplan bands at λλ4165, 4432 and 4728 appear readily and photographs and measurements made with large dispersion are presented. The measurements support Kaplan's vibrational analysis for these bands, but it is believed that other bands in the ultra-violet belong to a different system. The rotational structure and probable type of electronic transition are discussed.

A weak new system of bands in the Green has been observed. A provisional analysis gives $\omega_{\frac{1}{2}}'=896$, $\omega_{\frac{1}{2}}''=740$ cm.$^{-1}$.

The electronic levels of N_2, the effect of excitation conditions on the band systems of N_2, and the bearing of the results on the determination of the dissociation energy are discussed.

§ 1. INTRODUCTION

Investigations on the N_2 spectrum were commenced with a view to obtaining further information about the dissociation energy of this molecule. The reasons for doubting the value of 7·38 ev. have been given briefly by Gaydon and Penney (1942) and will, it is hoped, be published in detail at a later date. While attempting to photograph the Vegard-Kaplan bands in a silent, ozonizer-type discharge as recommended by Wulf and Melvin (1939), some unfamiliar bands in the blue and green regions were observed. The bands in the blue, which are degraded to the red, were apparently first observed by Goldstein (1905) and have since been obtained under small dispersion by Kaplan (1934) and Hamada (1937).* The bands in the green are degraded to the violet and are apparently a new system.† A preliminary note on these bands has already appeared (Gaydon, 1943 a), and new singlet systems of N_2 in the ultra-violet, which were discovered during these investigations, have been fully reported (Gaydon, 1943 b).

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* I am indebted to Prof. G. Herzberg for supplying this reference, which I had previously overlooked.

† A recent note by Kaplan and Rubens (1941) reports five new bands between 5000 and 6100 A. in a weak discharge through nitrogen; no measurements were made; the bands were provisionally assigned to N_3 or a triatomic oxide of nitrogen.

The bands in the blue, the Goldstein-Kaplan bands as they have been called, occur quite strongly in normal discharge-tube sources provided the gas pressure is relatively high, and it is surprising they are not better known. No photographs or detailed description of the bands appear to have been published and they are not mentioned in many of the recent books on band spectra. Kaplan has provisionally assigned the bands to a transition to the $B\,^3\Pi$ state of N_2, but the intensity distribution and limited accuracy of the available measurements did not, in the author's opinion, carry conviction that this analysis was necessarily correct. In this paper photographs under large dispersion and more detailed discussion of the Goldstein-Kaplan bands and the new Green system are presented.

§ 2. EXPERIMENTAL

The bands were first obtained with the ozonizer-type discharge. For this, two concentric glass tubes about a metre long were used, the inner tube having an external diameter of about 0·8 cm., and the outer tube having a bore of 1·4 cm. The inner tube was filled with a conducting liquid which served as one electrode, while a covering of tin-foil around the outer tube acted as the other electrode. A fairly fast stream of nitrogen from a cylinder was admitted through a side tube to the space between the concentric tubes at one end, which was closed, and the gas passed out into the air at atmospheric pressure at the open end. A silent discharge was maintained with an induction coil, and the violet glow was viewed end-on through the open end. This source brought out the Goldstein-Kaplan bands and the Green system quite well relatively to the other systems of N_2, but the intensity was insufficient for work with large dispersion.

In order to study the structure of the bands in greater detail, experiments were made with various designs of discharge tube and under various conditions of excitation. It was found that the Goldstein-Kaplan bands appeared quite readily in an ordinary induction-coil discharge through nitrogen (but not air), provided the gas pressure was fairly high (a few cm. of mercury). At lower pressure the spectrum was dominated by the Second Positive and First Positive bands, and the Goldstein-Kaplan bands were relatively very weak. These bands were never observed well in a transformer discharge, probably because the transformers used did not give a sufficiently high voltage to strike the discharge at the desired high pressure. The Goldstein-Kaplan bands are, however, present on some plates taken by Dr. R. W. B. Pearse using a discharge maintained by a valve oscillator. The new Green bands were not observable with the ordinary induction-coil discharge as the very strong First Positive bands masked this region of the spectrum.

The bands were obtained in various designs of discharge tube, but it was found that to obtain high intensity for work with large dispersion a small-bore tube was best. The tube used for later work had a central capillary of about 2 mm. bore and was 20 cm. long, the discharge being viewed end-on through one of the electrodes which had the form of a hollow cylinder. Several plates were taken with a glass-prism spectrograph giving moderate dispersion, and by reducing the pressure of nitrogen slightly below the optimum so as to increase the brightness of the discharge, satisfactory spectrograms of the 4728-A. band were obtained in the second order of the 6-m. concave grating of the Physics Department, this giving a dispersion of 1·9 A./mm. One of these spectrograms is reproduced as (*d*) in the plate.

By far the purest source for both the Goldstein-Kaplan and the new Green system was found to be a Tesla-coil discharge, again at relatively high pressure. A commercial " leak-tester " was used as the Tesla coil, and the same capillary discharge tube was found satisfactory. In this source the First Positive bands were, for some reason, largely suppressed, and it was found possible to obtain useful spectrograms showing the new Green system. Some of these, taken with a glass-prism instrument, are reproduced in the plate, (*a*), (*b*), (*c*).

For the early experiments, commercial nitrogen containing traces of oxygen and moisture was used, and the spectrum showed quite strong NO and OH bands in addition to N_2.

Experiments were carried out with various gas mixtures in order to obtain chemical evidence on the emitting molecule. With special, chemically dry, oxygen-free nitrogen as supplied by British Oxygen Co., the Goldstein-Kaplan and Green systems were well developed and the NO and OH bands were very weak, although admittedly not quite absent. With exactly similar discharge conditions, but using air instead of nitrogen, the Goldstein-Kaplan and Green bands were entirely absent; the NO and OH were of course strong. With air it was also noticed that the N_2 First Positive bands were much less intense than in the discharge through pure N_2: reference is made later to this effect. To check that the new bands were not due to some unknown impurity in the cylinder nitrogen, atmospheric nitrogen, prepared by absorbing the oxygen with alkaline pyrogallol, was used, and it was found that the new bands appeared satisfactorily. All the chemical evidence, therefore, suggests N_2 as the emitter of the band systems studied.

Using the specially pure nitrogen, small additions of oxygen, water vapour and hydrogen were made. It was found that even very small quantities of oxygen had a marked effect in reducing the intensity of both the Goldstein-Kaplan bands and the Green system. Less than 10 % of oxygen was sufficient to remove all trace of the bands. Water vapour also had a marked inhibiting effect, and nitrogen saturated with moisture at room temperature (about 2 % H_2O) showed the bands only very weakly. Hydrogen also had an inhibiting action, but less strong; with nitrogen which contained a trace of oxygen, the addition of a little hydrogen appeared to strengthen the bands, probably because it converted the oxygen to water, so reducing the inhibiting action of the oxygen. Discharges through flowing nitrous oxide did not show the bands.

§3. THE GOLDSTEIN-KAPLAN BANDS

Goldstein (1905) originally published a brief description and rough wavelengths of some bands in the blue. Kaplan (1934, 1935) rediscovered these bands in the blue and also recorded bands around 3180, 3114, 3027, 3010 and 2886 A. He suggested that they were due to N_2 and involved a transition to the B $^3\Pi$ state of this molecule, high vibrational levels of this state being involved. Hamada (1937), in a paper on metastable nitrogen, records having observed the bands in the afterglow and gives the following wave-lengths: 2863·5 (0, 2), 3005·4 (0, 3), 3159·2 (0, 4), 3326·1 (0, 5), 3504·0 (0, 6), 3707·1 (0, 7), 3925·4 (0, 8), 4166·0 (0, 9), 4432·2 (0, 10), 4728·0 (0, 11), 5058·6 (0, 12), 3025·8 (1, 4) and 3178·4 (1, 5), noting that the last two were very weak, but giving no other information about the relative intensity of the bands.

In the present investigations only the bands around the blue region are well developed. The strongest three bands have first heads at 4165, 4432 and 4728 A., and there are weaker bands at 5059 and around 5450. These bands are shown in the plate, which reproduces spectrograms of the Tesla discharge through nitrogen and through air, (*a*), (*b*) and (*c*), with the glass-prism spectrograph, and (*d*) an induction-coil discharge through nitrogen and through air taken in the second order of the 6-m. concave grating.

The structure of the individual bands is obviously rather complex, each band showing a number of heads and outstanding features. Three of the clearest heads have been selected for each band where possible and measured. These measurements are presented in table 1.

Table 1

Wave-lengths (in air) and wave-numbers (*in vacuo*) of the Goldstein-Kaplan bands

λ	ν	λ	ν
4165·7	23998·8	5059·4	19760
4171·6	23964·8	5066·7	19731
4178·2	23927·0	5076·2	19694
4432·3	22555·0	—	—
4438·8	22522·5	—	—
4446·2	22484·7	5450	18340
4728·4	21143·0		
4735·6	21110·7		
4743·8	21074·3		

The 4165-A. band is rather badly overlapped by the (2, 6) Second Positive band, perturbations in the rotational structure of the latter producing intensity anomalies which confuse the appearance of the head of the 4165-A. band; by careful comparison of N_2 and air plates it has been possible, however, to pick out the three heads selected for measurement with fair certainty. The heads of the 4432-A. band are fairly free from overlapping structure, but the tail of this band is overlaid by stronger Second Positive structure. The 4728-A. band, being the most nearly free from overlapping, was selected for more detailed study with large dispersion. The 5059-A. band presents rather a confused appearance, which is probably caused by superposition by a band of the Green system. The 5450-A. band is definitely present and shows up clearly on small-dispersion spectrograms taken with the ozonizer-type discharge, but has not been photographed well with larger dispersion; location of heads is therefore difficult.

The rotational structure of the 4728-A. band is fairly well resolved on the grating spectrogram (strip (*d*) of plate). The magnitude of the structure is consistent with N_2 as the emitter. Much time has been spent in attempting a full rotational analysis, but without success. Some fragmentary branches have been picked out, these showing fairly large second differences of about 0·7 cm.$^{-1}$, indicating that $B''-B'$ may be of the order 0·35 cm.$^{-1}$. All the branches are much overlaid by other structure, however, and do not run smoothly for more than seven or eight members: it is very probable that the levels are perturbed. There are some signs that the fragmentary branches show the alternation of intensities characteristic of a homonuclear molecule when a Σ level is involved, but the overlapping and uncertainty about the reality of some of the branches make it unsafe to rely on this doubtful observation.

The complexity of the rotational structure obviously rules out a transition between singlet states, and doublet states (for N_2^+) are also almost certainly eliminated. It also seems certain that there are Q-type branches of considerable strength, indicating that there is a change of Λ and so ruling out $\Sigma\rightarrow\Sigma$ or $\Pi\rightarrow\Pi$ transitions. The general appearance of the band seems consistent with a transition between a $^3\Sigma$ and a $^3\Pi$ state, or perhaps between $^3\Pi$ and $^3\Delta$. It is possible that quintet states are involved, but these seem less likely than triplets.

The bands in the blue region which have been described obviously lie in a single progression and, according to Kaplan's analysis, are the (0, 9) to (0, 13) bands of a transition to the B $^3\Pi$ state of N_2. The wave-number intervals between the bands, about 1443, 1411, 1381 and 1354, do, indeed, agree well with the values 1443, 1413, 1383 and 1353 for the B $^3\Pi$ level, as obtained from measurements of the First Positive bands. The present measurements therefore support Kaplan's analysis of the bands in the blue region, although it must always be remembered that it is never very difficult to force a small group of converging wave-numbers to fit at some point with those of another group; the values of $x_e\omega_e$ are often about the same for the several electronic states of a molecule, and close agreement of the two groups of intervals may then easily be fortuitous.

Apart from the bands around the blue region listed in table 1, spectrograms of the ordinary induction-coil discharge at relatively high pressure show a weak but undoubtedly real band around 3007 A. (the head is rather difficult to locate), but, despite careful scrutiny of plates taken with a large quartz (Hilger E.1) spectrograph, none of the other bands listed by Kaplan or Hamada has been observed. The region is, of course, heavily overlaid with strong Second Positive bands, but it is certain that, if present at all, these bands, assigned to the Goldstein-Kaplan system, are very weak under these conditions of excitation.

If we accept the vibrational analysis for the strong blue bands as (0, 9) to (0, 13), and remember that the rotational structure indicates that the bands are strongly degraded to the red (and therefore correspond to a marked decrease in internuclear distance during the transition), application of the Franck-Condon principle, or a more refined wave-mechanical treatment, indicates that bands such as (0, 2) and (0, 3) would not be of appreciable intensity. This difficulty seems serious and is fundamental to Kaplan's analysis, which includes the blue and the ultra-violet bands in the same progression; raising the value of v' would only lead to still greater difficulty in explaining the intensity distribution. The author is therefore of the opinion that the bands observed by Kaplan and Hamada around 2800 to 3200 belong to a different system. This is supported by Kaplan's statement (1934) that " The first three bands [the blue ones] were observed only at pressures below 0·1 mm., while the other two [3010, 2864] were present at all pressures." This statement and the weakness of the ultra-violet group in the author's investigations seem to prove that the two groups require slightly different experimental conditions, and cannot therefore have the same initial levels. The paradox is the apparent observation of the whole progression by Hamada (1937), but in the absence of photographs or details it is uncertain how much reliance his observations should command. It is probable that the Goldstein-Kaplan bands should be regarded as two systems, one in the ultra-violet and the other in the blue region, this latter being due to a transition from a $^3\Sigma$, or possibly a $^3\Delta$, level to the B $^3\Pi$ state of N_2.

§ 4. THE GREEN SYSTEM

These bands occur in the ozonizer-type discharge at atmospheric pressure and in the Tesla discharge at a pressure of a few cm. of mercury; with an ordinary induction-coil or transformer discharge, even at high pressure, the new bands, if present, are entirely masked by strong First Positive bands. When the " buzzer" of the induction coil is adjusted to give a very feeble discharge, which is violet instead of bronze in colour, the Green bands are faintly visible among those of the First Positive system. The conditions of excitation required to bring up the Green system are, therefore, very similar to those required for the blue Goldstein-Kaplan bands, but on some plates there appear to be changes in the relative intensity of the systems; this may indicate that their initial electronic levels are not the same.

The Green bands are degraded to the violet and their structure is again complex. For the bands which have been measured (see table 2) five heads or outstanding features have been selected, of which the last (of shortest wave-length) is the strongest and most reliable; there are at least two other weak heads in front of the first measured head. There is a strong band with its strongest (fifth) head at 5309 A., and a second band which is nearly as strong at λ5574. Comparison of the intensity of these two bands is made difficult by rapid change of plate sensitivity with wave-length in this region. With heavy exposure a much weaker band, definitely of the same type, having its strongest head at 5270 A., is visible. There is another fairly strong band, which is probably of the same type, with its strongest head at 5815 A., but this is heavily overlaid by First Positive bands, and location of heads is difficult. There is some complex band-structure between 5040 A. and 5080 A.; part of this is due to a blue Goldstein-Kaplan band, and there is also a weak Second Positive (3, 10) head at 5067 A., but some of the structure appears to be attributable to a band of the Green system; its strongest head *might* be at 5073 A. (19707 cm.$^{-1}$). There are indications of other very weak bands lying to longer wave-lengths, around 6075 A. (16457 cm.$^{-1}$) and 6340 A. (15768 cm.$^{-1}$), but these are masked by First Positive bands.

The vibrational structure of the bands of the Green system is not very obvious, but a provisional scheme is set out in table 3. It must be emphasized that measurements of bands other than those given in table 2 are very uncertain, and the provisional scheme is not necessarily correct. It has the advantage that it sets the three strongest bands as the (1, 0), (0, 0) and (0, 1), but the vibrational frequency intervals at $\omega_{\frac{1}{2}}' = 896$ cm.$^{-1}$ and $\omega_{\frac{1}{2}}'' = 740$ cm.$^{-1}$ are rather small for N_2; however, it is known (Chulanovskii, 1935) that the $b'\,^1\Sigma^+$ level of N_2 has a value for ω_0 of only 758·6.

Table 2

Wave-lengths and wave-numbers of heads of bands of the Green system

λ	ν	λ	ν
5289·2	18901	5595·0	17868·2
5283·1	18923	5587·6	17891·8
5278·6	18939	5582·9	17906·9
5274·4	18954	5579·3	17918·3
5270·5	18968	5574·8	17932·9
5326·9	18767·2	5839·5	17120
5320·7	18789·4	—	—
5316·7	18803·4	—	—
5312·9	18817·0	—	—
5309·5	18828·8	5814·7	17193

The rotational structure of the 5309 A. band is partially resolved, although not sufficiently so to justify an attempt at full analysis. The general appearance of the band is very similar to that of the Fourth Positive bands of N_2 (for photographs of these under fairly large dispersion see Gaydon, 1943 b). This suggests that the band may be due to a transition between a $^3\Sigma$ and a $^3\Pi$ state. It is possible to imagine that the band shows branches with alternating intensities, this supporting the assignment to N_2 and the provisional conclusion that a Σ state is involved (transitions involving only Π and Δ states do not usually show alternating intensities because of unresolved Λ doubling).

Table 3. Provisional vibrational scheme for the Green system

v' v''	0		1		2		3
0	17933	740	17193	736	(16457)*	689	(15768)*
	896						
1	18829						
	878						
2	19707	739	18968				

* These measurements are rough estimates of the centres of the bands ; the strongest heads probably lie to slightly greater wave-numbers.

§ 5. DISCUSSION

The electronic energy levels of N_2. The types of source used for the production of these systems of N_2 are all characterized by fairly mild excitation conditions. In all the sources, the First Negative bands of N_2^+ are weak and there is no sign of the N_2 systems involving highly excited states such as the Fourth Positive. The use of a mild condensed discharge instead of the uncondensed one does not enhance the Goldstein-Kaplan or new system; rather the contrary. The indications are, therefore, that the electronic levels involved are of comparatively low energy.

No other system involving the upper level of the blue Goldstein-Kaplan bands appears to be known, and, if the provisional analysis for the Green system is correct, this indicates the existence of two more low-lying electronic levels of N_2 with which no other combinations are known. This at first appears rather surprising, but becomes less so if we compare the spectrum of N_2 with that of the iso-electronic molecule CO.

For CO the two triplet systems of lowest excitation energy, the Asundi bands and the "Triplet" bands, are both weak and far from prominent under ordinary conditions of excitation, which bring up much more strongly the more highly excited Third Positive, "3A", and Ångstrom systems. It may well be, therefore, that some of the systems of N_2 requiring low excitation energy are also abnormally weak. For CO the possible transitions $b\,^3\Sigma^+ \rightarrow a'\,^3\Sigma^+$ and $c\,^3\Pi \rightarrow a'\,^3\Sigma^+$ have not been recorded. This suggests that, for N_2, transitions between the new levels and the better known levels may also fail to appear, especially as, for N_2, additional selection rules ($g \neq g$, $u \neq u$) due to the symmetry properties of the homonuclear molecule will impose additional restrictions on the number of possible transitions.

For CO, the weakness of the Asundi and "Triplet" systems and failure to observe the other possible transitions is largely the result of the Franck-Condon principle. The $a'\,^3\Sigma^+$ state has a much smaller ω and therefore almost certainly a much greater internuclear separation than the other electronic states; this results in small overlap of the wave-functions of $a'\,^3\Sigma^+$ with those of the other states and, therefore, the low or negligible intensity of the systems. We have seen that for the Green system of N_2 there are indications of ω_1 values as low as 896 and 740 cm.$^{-1}$, which are both very much smaller than for any other known triplet level. For the Goldstein-Kaplan band of 4728 we have seen that there are indications from the rotational structure that $B''-B'=0{\cdot}35$; combining this with the value of B_{11}'' (estimated from molecular constants for the $\mathrm{B}\,^3\Pi$ state as $1{\cdot}41$) we arrive at $B'=1{\cdot}1$ cm.$^{-1}$. This is about the same as that of the $b'\,^1\Sigma_u^+$ state of N_2 which has $B=1{\cdot}14$ and $\omega_0=758$. Thus, by analogy with CO, the failure to observe other transitions to the electronic states of N_2 involved in the Green and Goldstein-Kpalan systems is not so surprising after all.

Apart from these considerations, other evidence suggests that there are some hitherto unknown triplet levels of N_2. The $\mathrm{C}\,^3\Pi_u$ upper level of the Second Positive bands shows perturbations which prove the existence of a stable $^3\Sigma_u^-$ state, causing the perturbations in the $v=1$ and 4 levels, and probably of another $^3\Pi_u$ state causing weaker perturbations (Gerö, 1935). It is not improbable that one of these perturbing levels may be involved in the emission of the Green system.

The conditions of excitation. The new systems only appear under rather limited excitation conditions, and it would seem to be of interest briefly to discuss this aspect of the subject. The detailed processes taking place in discharge tubes are not well understood, and the author has not seen a completely satisfactory explanation, even of such striking effects as the variation of the relative intensity of the First and Second Positive systems of N_2 with discharge-tube conditions;

a transformer or high current-density induction-coil discharge through nitrogen is orange in colour, the First Positive being very strong, while electrodeless or very low current-density induction-coil discharges are blue-violet in colour, the First Positive bands being very weak. The substitution of air for nitrogen in the transformer discharge also weakens the First Positive. It is probable that at least three factors—the nature of the exciting particles, the velocity of the exciting particles, and deactivation by collision—play an important part in determining the relative strength of the various band systems.

The exciting particles may be either electrons or heavier ions, and perhaps in rare cases light quanta. For electron excitation, as in the electron beam and, to a large extent, in ordinary discharges, we may expect the Franck-Condon principle to be obeyed, the N_2 molecule being excited only to states of nearly the same internuclear distance. For excitation by ions, as in canal rays, we may expect the collision process to transfer momentum as well as electronic energy, and systems and vibrational levels other than those conforming to the Franck-Condon principle may be excited. Smyth and Arnott (1930) have studied the vibrational intensity distribution among N_2 bands and found that most discharges approximate to electron excitation, but that the electrodeless discharge approaches most clearly, among the discharge types studied, to the canal-ray type. This would seem to suggest that, since the new bands appear best in the electrodeless ozonizer-type discharge and the Tesla discharge, they are favoured by ionic rather than electron-collision excitation, in agreement with the view expressed above that a big change in internuclear distance must take place. This is not, however, supported by the internal evidence of the spectra; the ozonizer and Tesla discharges show a low vibrational temperature for the Second Positive bands with the (0, 5) band much stronger than the neighbouring (4, 10) band, while the transformer discharge and low-pressure induction-coil discharges, which do not favour the new systems, show the (4, 10) band more strongly than the (0, 5), indicating a higher vibrational temperature.

It is also probable that the energy of the exciting electrons or ions is important. Little is known about the details of molecular excitation by controlled electrons, but for atoms (e.g., the work on cadmium by Larché, 1931) the curve of excitation probability versus electron velocity sometimes shows a quite sharp peak for partially forbidden transitions (e.g., Cd 3261 A., $^1S \rightarrow {}^3P$) compared with a slow rise to a flat maximum for allowed transitions (e.g., Cd 2288 A., $^1S \rightarrow {}^1P$). Similar effects probably occur for molecules. The high pressure favouring the new systems may act by reducing the mean free path of the electrons and so limiting the energies which they can attain before suffering collision.

Deactivation of electronically excited molecules by collision with other molecules must play a very important rôle in the emission of light from discharges. The First and Second Positive systems of N_2 are due to the transitions $B\,^3\Pi \rightarrow A\,^3\Sigma$ and $C\,^3\Pi \rightarrow B\,^3\Pi$ respectively, so that the final state of the Second is the initial state of the First Positive system. Were it not for deactivation by collision, the First Positive bands should therefore always be stronger than the Second, because any molecule which has just undergone the transition $C\,^3\Pi \rightarrow B\,^3\Pi$ must then be in a position to undergo the further transition $B\,^3\Pi \rightarrow A\,^3\Sigma$. In practice, however, it is possible to obtain discharges in which the Second Positive bands are strong and the First are almost absent, at least in the visible region. The reduction of intensity of the First Positive bands and the new systems by a little oxygen is probably a case of collision deactivation. It is usually assumed that the radiative lifetime of a molecule in an excited state is of the order 10^{-8} sec., but this is probably too short; Oldenberg and Rieke (1938) have shown that the radiative life of excited OH, corresponding to the very strong 3064-A. band, is $3{\cdot}8 \times 10^{-6}$ sec. For weaker transitions, it seems safe to assume a life of the order 10^{-6} or even 10^{-5} sec. At a pressure of a few cm. of mercury, each molecule will make over 10^8 collisions per sec., so that each excited molecule may make from 100 to 1000 collisions before radiating. Thus, if oxygen molecules have a very high efficiency for producing deactivation, there appears to be no difficulty in seeing how a few per cent of oxygen may weaken the emission of a particular band system.

Although the influence of three factors in modifying the emission spectrum of discharges has been discussed, it is not possible to say quantitatively which is the most important for the present experiments. More work on the processes of excitation in electrical discharges seems desirable.

The dissociation energy. The discovery of the new Green system has no direct bearing on the determination of the dissociation energy of N_2. No fresh predissociations have been observed and no further extrapolations of vibrational levels to their dissociation limits are possible.

The evidence for the existence of some new electronic levels of N_2 of low energy, possibly levels of $^3\Pi$ type, has, however, an indirect bearing on the problem. In applying the non-crossing rule, that potential-energy curves for molecular states of the same species cannot cross, the $B\,^3\Pi_g$ state presents some difficulty as a large number of vibrational levels are known, and since this state should, if it is the lowest of its type, dissociate to the lowest possible products, namely, $^4S + {}^2D$, it is necessary to assume either a very high dissociation energy or that the potential curve for $B\,^3\Pi_g$ has a pronounced maximum. Now, however, the discovery of the new levels opens up the possibility of there being a $^3\Pi_g$ level below $B\,^3\Pi_g$ which could then dissociate to $^4S + {}^2P$, which would present less difficulty.

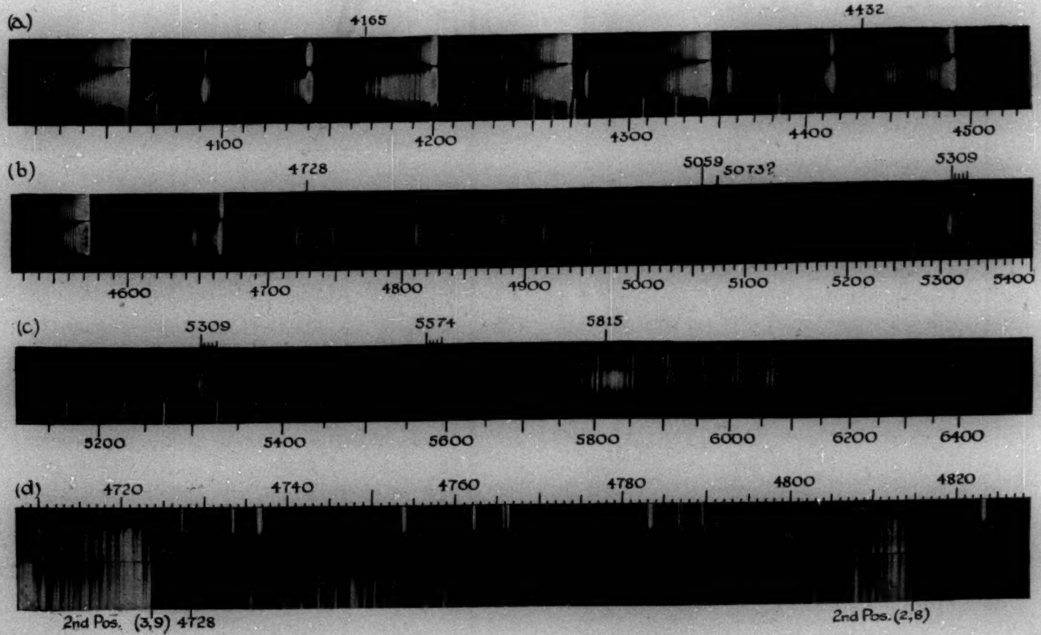
In conclusion, I wish to express my sincere thanks to Sir Alfred Egerton for his keen interest in these investigations, and to the Council of the Royal Society for financial assistance.

DESCRIPTION OF PLATE

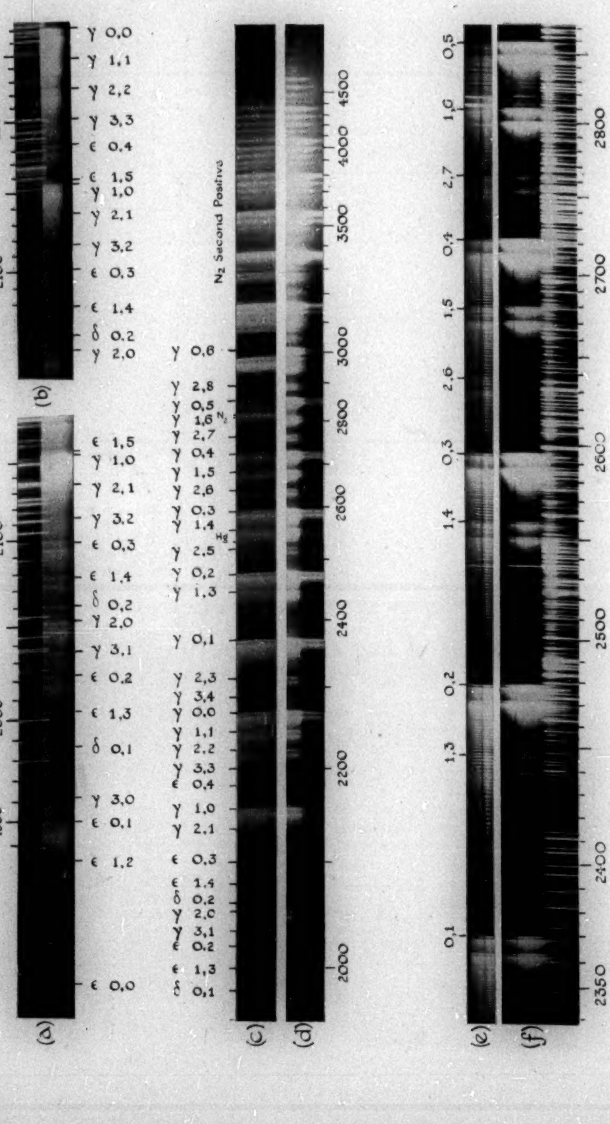
(*a*), (*b*) and (*c*) are enlargements of spectrograms taken with a Tesla coil discharge at relatively high gas pressure (about 10 cm.) on a glass-prism spectrograph. In each case the upper spectrum is of a discharge through air, showing N_2 Second Positive, First Positive and weak N_2^+ bands. The lower spectrum is of the discharge through pure nitrogen and shows the Goldstein-Kaplan and new Green bands in addition. An iron-arc comparison spectrum is shown in each case. (*a*) and (*b*) were taken on a Kodak O.H. plate with an exposure of 1 hr. (*c*) was taken on an Ilford H.P.2 plate; exposure 1 hr.

(*d*) Spectra of an induction-coil discharge at a pressure of about 1 cm. mercury, photographed in the second order of a 6-m. concave grating. The upper spectrum is of a discharge through air, with an iron-plus-manganese-arc comparison, while the lower spectrum is of the discharge through pure nitrogen and shows the 4728-A. Goldstein-Kaplan band. Ilford Press Ortho 2 plate; exposure 12 hrs.

The band spectrum of N_2: weak systems in the visible region



The band spectrum of NO: the gamma and epsilon systems



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THE BAND SPECTRUM OF NO: THE GAMMA AND EPSILON SYSTEMS

By A. G. GAYDON, D.Sc.,

Chemical Engineering Department, Imperial College, London, S.W. 7

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ABSTRACT. The spectrum of NO has been studied in a transformer discharge and in a silent ozonizer-type discharge. Bands of the γ, ϵ and δ systems have been photographed and measured. From the measurements and intensity distribution it is shown that the γ and ϵ systems are separate, this being contrary to Herzberg and Mundie's conclusion that the ϵ bands were part of the γ system. There is no evidence for predissociation in the γ or ϵ systems. It is difficult to reconcile the observations with a value for the heat of dissociation of NO as low as 5·29 ev.

§1. INTRODUCTION

Recently Gaydon and Penney (1943) have expressed doubts about determinations of the dissociation energies of CO, N_2 and related molecules, which are based on the observation of weak predissociations. For NO, the dissociation energy of which can be linked with that of N_2 by thermochemical data, no direct evidence of much value is available, but Herzberg and Mundie (1940) have suggested that the γ and ϵ band systems of this molecule are really one system, and that the greater strength of the ϵ system (or, on this suggestion, of bands of the γ system with $v' \geqslant 4$) in absorption is due to greater line breadth resulting from predissociation in these levels.

In their paper, Herzberg and Mundie state that "The observation of γ bands in emission with $v' > 3$ (Guillery, 1927), which would contradict our explanation, does not appear to be definite". In fact, there is no difficulty in observing the bands reported by Guillery, and in order to settle the point the author has thought it desirable to publish photographs of these bands.

Although many of the bands of the γ system have been studied in detail by Guillery (1927) and Schmid (1930), and the former has given a vibrational array for the combined γ and ϵ systems with head measurements to the nearest 1 A., and while Hellermann (1936) has measured some of the ϵ bands of the $v'=0$ progression from observations in emission from a high-frequency discharge, yet there does not appear to be any full record of reasonably precise measurements of the bands of these systems; the table of measurements collected by Pearse and Gaydon (1941) includes some very poor measurements, and is in many respects far from complete. The author has therefore thought it desirable to round off the observations on the ϵ system by presenting full measurements and estimates of intensities for all the bands of the γ and ϵ systems which have been observed.

§ 2. EXPERIMENTAL

The γ and ϵ bands of NO are emitted quite strongly by an ordinary electric discharge through air at reduced pressure. For most of the work a transformer discharge through a tube of the type described by Hunter and Pearse (1936) was used. This proved an intense source and enabled satisfactory spectrograms to be taken down to the limit of transmission of air with quite short exposures.

This transformer discharge at low pressure is, however, characterized by a rather high rotational temperature of the bands, the long rotational branches of the strong bands tending to obscure the heads of weak bands. It was found during the course of some investigations on the spectrum of nitrogen (Gaydon, 1944), using a silent (ozonizer-type) discharge through nitrogen at atmospheric pressure, that the NO bands were very prominent and that in this source the heads of the bands were very clear and outstanding owing to the low effective rotational temperature. This effect is clearly seen by comparison of strips (*e*) and (*f*) of the accompanying plate. This ozonizer discharge, the simple tube for which has been described in the paper on N_2 (Gaydon, 1944), using commercial nitrogen which contained a trace of oxygen as impurity, was therefore used for measurements of most of the γ bands. With this source, however, the ϵ system did not appear at all on any of the author's plates.

The strong bands of the γ system in emission lie in the ordinary quartz ultra-violet region of the spectrum and no difficulty was experienced in obtaining satisfactory photographs of these bands using a medium-sized quartz spectrograph (Hilger E.2). With the transformer discharge, exposure times were of the order of a few minutes; with the weaker ozonizer-type discharge, exposures of from $\frac{1}{2}$ to 6 hours were required.

Some of the γ bands and most of the ϵ system lie to rather shorter wavelengths and cannot be recorded with a medium-sized quartz instrument, but many of the bands were photographed quite readily with a small quartz spectrograph, the dispersion of which in this region (1900–2100 A.) is adequate for examining the vibrational structure. When using the small instrument the slit was placed close against the source and no condensing lens was used. In this way the atmospheric path length was kept to a minimum, and so the absorption by oxygen was reduced. No O_2 bands at wave-lengths greater than 1940 A. were observed; the (0, 0) ϵ band at 1880 A. was recorded on the plates, but oxygen absorption was present in this region, and no measurements were made below 1940 A. For work below 2300 A., special ultra-violet-sensitive plates were used.

For wave-lengths greater than 2100 A., an ordinary iron-arc comparison spectrum was used. Between 2100 and 1944 A., a copper spark (condensed induction-coil spark between copper electrodes) was employed, standards quoted by Burns and Walters (1931) being available.

§ 3. THE MEASUREMENTS

The bands of both systems are double double-headed. For most of the bands the author has measured all four heads (P_1, Q_1, P_2, Q_2),* but only the P heads are included in the tables. These are usually easier to measure and more reliable than the Q heads, whose exact position is sometimes confused by lines of the P branches. The Q heads lie to the short wave-length side of the P heads, by about 1·5 A., at the long-wave end, and about 0·8 A. at the short-wave end (around 1950 A.). For the bands of the γ system, which have been the subject of rotational analysis by Guillery or Schmid, their measurements made under larger dispersion are given instead of the author's. For the ϵ system the P_1 heads of three bands measured by Hellermann (1936) are included. This table also includes a provisional value for the P_1 head of the (3, 0) band; this is derived by adding 4 A. to Leifson's value (1926) for the centre of the band as observed in absorption, since it has been observed that his "centres" differ from Hellermann's heads by about this amount.

The measurements for the γ and ϵ systems are given in tables 1 and 2. The reasons for believing that the systems are separate, and not one as suggested by Herzberg and Mundie, are given below. For bands of reasonable intensity lying to wave-lengths greater than 2200 A., which have been measured with the E.2 instrument, the probable error of the measurements is about 2 cm.$^{-1}$. For bands below 2200 A. and a few of the weaker bands to longer wave-lengths, which were measured on the small quartz instrument, the probable error is about 5 cm.$^{-1}$.

Table 1. The P_1 and P_2 heads* of the γ system of NO

v', v''	λ_{air}	$\nu_{\text{vac.}}$	v', v''	λ_{air}	$\nu_{\text{vac.}}$
0, 6	3008·8	33226	0, 1	2370·2	42178
	2997·6	33350		2363·3	42301
1, 7	2952·0	33866	2, 3	2316·3	43159
	2941·9	33982		2309·5	43286
2, 8	2898·3	34493	3, 4	2289·8	43659
	2888·2	34613		2284·1	43768
0, 5	2859·5	34961	0, 0	2269·4	44051
	2849·8	35080		2262·8	44179

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* This is the notation used by Guillery and Schmid ; these are really the ${}^{O}P_{12}$, P_2, P_1 and Q_1 heads respectively in modern notation.

Table 1 (*continued*)

v', v''	λ_{air}	$\nu_{\text{vac.}}$	v', v''	λ_{air}	$\nu_{\text{vac.}}$
1, 6	2810·4	35573	1, 1	2245·4	44522
	2800·8	35694		2239·4	44640
2, 7	2763·7	36173	2, 2	2222·4	44982
	2755·2	36284		2216·3	45105
0, 4	2722·2	36724	3, 3	2199·6	45448
	2713·2	36845		2194·0	45565
1, 5	2680·0	37302	1, 0	2154·9	46391
	2671·4	37423		2149·1	46516
2, 6	2639·1	37880	2, 1	2135·0	46824
	2630·7	38001		2129·6	46943
0, 3	2595·7	38514	3, 2	2115·0	47266
	2587·5	36636		2109·5	47390
1, 4	2559·0	39067	2, 0	2052·8	48699
	2550·0	39189		2047·5	48824
2, 5	2523·6	39614	3, 1	2035·7	49107
	2516·4	39727		2030·7	49228
0, 2	2478·7	40332	3, 0	1961·1	50975
	2471·1	40455		1956·1	51106
1, 3	2447·0	40855			
	2440·0	40972			

Table 2. The P_1 and P_2 heads* of the ϵ system of NO

v', v''	λ_{air}	$\nu_{\text{vac.}}$	v', v''	λ_{air}	$\nu_{\text{vac.}}$
0, 4	2181·8	45820	0, 1	1949·7	51272
	2176·1	45938		1945·0	51398
1, 5	2157·5	46336	0, 0		53147†
	—	—			—
0, 3	2099·8	47608	1, 0		55424†
	2094·5	47730			—
1, 4	2078·2	48119	2, 0		57657†
	2073·0	48224			—
0, 2	2022·3	49431	3, 0		(59844)‡
	2017·5	49551			—
1, 3	2003·6	49895			
	1998·6	50018			

* See footnote on previous page.
† Measurement by Hellermann.
‡ Measurement from Leifson (see text).

Table 3. Combined vibrational schemes for the P_1 heads of the γ and ϵ systems of NO

v_γ' \ v''	0		1		2		3		4		5		6		7		8
0	44051		42178		40332		38514		36724		34961		33226				
		1873		1846		1818		1790		1763		1735					
	2340		2344				2341		2343		2341		2346				
1	46391		44522				40855		39067		37302		35572		33866		
		1869						1788		1765		1730		1706			
	2308		2302				2304				2312		2308		2307		
2	48699		46824		44982		43159				39614		37880		36173		34493
		1875		1842		1823						1734		1707		1680	
	2276		2283		2284		2289										
3	50975		49107		47266		45448		43659								
		1868		1841		1818		1789									
v_ϵ'	(2172)		(2165)		(2165)		(2160)		(2161)								
0 (4)	H 53147		51272		49431		47608		45820								
		1875		1841		1823		1788									
	2277						2287		2282								
1 (5)	H 55424						49895		48102		46336						
								1793		1766							
	2233																
2 (6)	H 57657																
	2187																
3 (7)	(59844)																

In addition to the γ and ϵ bands, two other bands of similar but slightly different appearance are present on spectrograms of the transformer discharge. These are apparently bands of the δ system, the measurements agreeing with those given by Knauss (1928):

v', v''	λ_{air}	$\nu_{\text{vac.}}$	v', v''	λ_{air}	$\nu_{\text{vac.}}$
(0, 2)	2060·9	48507	(0, 1)	1985·4	50353
	2055·9	48624		1980·5	50475

These two bands of the δ system appear to have been erroneously included in the γ system by Guillery, who gives 2060 A. and 1984 A. for the (2, 0) and (6, 4) γ bands.

§ 4. THE VIBRATIONAL SCHEMES

The vibrational schemes for the γ and ϵ systems are set out in combined form in table 3. The P_1 heads have been used, as measurements of these heads only are available for a few bands, and in most cases it is probable that these first heads, being free from overlapping by other branches, yield the most reliable measurements. The error introduced by using head measurements instead of origins is, for these systems, quite small, as the author's measurements show that the separation between the P heads and the Q heads, which latter must coincide very nearly with the origins, is very constant, departing little from a mean value of about 20 cm.$^{-1}$; only for the (3, 0) γ band (P_1 50975, Q_1 51001 cm.$^{-1}$) does the variation of B with v result in a significant variation of the separation of the P_1 and Q_1 heads.

In table 3 the wave-number intervals between the band-heads are printed in small type. These intervals should correspond closely to those between the vibrational levels, i.e. to $\Delta G'(v+\frac{1}{2})$ and $\Delta G''(v+\frac{1}{2})$. The approximate constancy of these values shows that the scheme is fundamentally correct and that the measurements are fairly reliable. The roughly weighted average values for $\Delta G'(v+\frac{1}{2})$ are listed in table 4, allowance being made in the averaging for the probable accuracy of measurement of the individual bands involved.

Table 4. Wave-number intervals between the upper vibrational levels

v_γ'	0	1	2	(3)	(4)	(5)	(6)
v_ϵ'					0	1	2
$\Delta G'(v+\frac{1}{2})$	2342	2309	2279	(2162)	2280	2233	2187

It will be seen that there is a sharp break in these values, corresponding to the change from the γ to the ϵ levels. It is unlikely that a break of this magnitude is due, as suggested by Herzberg and Mundie, to a perturbation, and it must be taken as evidence for regarding the γ and ϵ systems as separate. This receives confirmation from other considerations discussed in the next section.

It is now possible to derive values for some of the molecular constants for the D $^2\Sigma$ upper electronic state of the ϵ bands and for the A $^2\Sigma$ upper state of the γ bands. The Q_2 heads of the bands must lie very near the origins, and for the (0, 0) γ band and the (0, 1) ϵ band, which are strong and favourably situated for careful measurement, these heads are at 44198·1 and 51418 cm.$^{-1}$ respectively.

Using these values and those for $\Delta G'$ given above, the constants listed in table 5 are derived. Although only expressed to the nearest cm^{-1}, these should be more reliable than any hitherto published.

Table 5. Molecular constants for the D $^2\Sigma$ and A $^2\Sigma$ states of NO

	ν_0	ν_e	ω_e	$x_e\omega_e$
D $^2\Sigma$	53293	53083	2327	23
A $^2\Sigma$	44198	43965	2374	16

§ 5. THE INTENSITY DISTRIBUTION

The vibrational intensity distribution among the γ and ϵ bands is interesting Strips (*c*) and (*d*) of the plate show the whole spectrum as obtained with the transformer discharge and with the ozonizer-type discharge, and, although in rather poor focus at the red end, serve to show clearly the main features of the intensity distribution in these sources.

The intensities of the bands in both sources have been estimated visually on an arbitrary scale of 10; dashes, –, are used to denote bands which, although favourably situated for observation, are negligibly weak. Apart from random errors of judgment in making the estimates, there may be slight systematic errors due to the necessity of using a quartz condensing lens in front of the slit for the ozonizer discharge, while for the more intense transformer discharge this was, as already explained, dispensed with; thus, for the ozonizer discharge there was a rather long air path, the oxygen absorption in which may account for the low intensity of the (3, 0) γ band in this source; the chromatic aberration of the condensing lens may also have the effect of favouring one region of the spectrum slightly at the expense of another region. Nevertheless, these estimates, which are set out in arrays in table 6, give a clear impression of the general trends.

Table 6. Vibrational intensity distribution

(*a*) Transformer discharge

v_ϵ'	v_γ' \ v''	0	1	2	3	4	5	6	7	8
	0	8	10	10	9	8	7	4		
	1	7	3	–	3	4	5	5		
	2	4	1	3	2	–	1	3	3	2
	3	2	2	½	1	2				
0	(4)	3	4	3	3	3				
1	(5)	HL		½	1	3	½			
2	(6)	HL								
3	(7)	L								

(*b*) Ozonizer discharge

v_γ' \ v''	0	1	2	3	4	5	6	7	8
0	8	10	10	9	8	7	5		
1	6	4	–	4	5	5	4	4	
2	3	1	3	3	–	2	3	4	3
3	½	1	½	1	2	½			
4			–	–	–				

H = observed in emission by Hellermann.
L = observed in absorption by Leifson.

Let us consider first the ozonizer source, as this brings up only the γ bands (v' 0 to 3). The strongest bands lie on a normal, rather open, Franck-Condon parabola. The plate shows strikingly the absence of the (1, 2) and (2, 4) bands and the presence of bands at (2, 2), (2, 3) and (3, 4), which lie right off the main parabola. To explain these details of the intensity distribution it is necessary to resort to a wave-mechanical treatment such as that carried out for the RbH spectrum by Gaydon and Pearse (1939). A similar treatment has been applied qualitatively to the NOγ system by sketching in approximate wave-functions and studying diagrammatically the overlap between the wave-functions of the various vibrational levels. It is clear that the observed distribution of intensity among the bands, as set out in table 6 (*b*), is in agreement with that to be expected. For RbH it was possible to indicate secondary and tertiary parabolae as loci of fairly strong bands lying off the main Franck-Condon parabola. For NO, however, the potential energy curves come more nearly above each other, and the overlap between the wave-functions of the various vibrational levels of the two electronic states is less simple than for RbH; and the loci of the bands falling off the main parabola form a more complex pattern which cannot be readily represented in a diagram.

The ordinary transformer discharge shows a very similar intensity distribution for the bands of the γ system, although the higher effective rotational temperature in this source, as already remarked, tends to obscure the heads of some of the weaker bands and rather alters the general appearance of the system. Apart from this difference, due to temperature, the striking difference between the transformer and ozonizer sources is the appearance of the ϵ bands and the two δ bands in the former source. This may be seen by comparison of strips (*c*) and (*d*) of the plate.

The bands of the $v'=0$ progression of the ϵ system are all definitely stronger than those of the $v'=3$ progression of the γ system, and it is clear from inspection of table 6 (*a*) that it would be impossible to explain the intensity distribution satisfactorily in terms of one system. If the γ and ϵ systems are treated separately, then both have a satisfactory distribution, the ϵ system again showing a rather open Franck-Condon parabola as locus of its strongest bands.

This separation of the bands into two systems is supported by the fact that, in the ozonizer, only the γ bands appear, while the transformer discharge yields also the ϵ and δ. It would require a very artificial explanation to account for the excitation of vibrational levels up to but not beyond $v'=3$ in one source, but up to 5 in another source.

The two δ bands are definitely present in the transformer discharge, but are not very strong. This system requires lower excitation energy than the ϵ system and, since it involves a very similar change of internuclear distance during the electronic transition, it might be expected to appear the more strongly of the two. The plates show, however, that the ϵ system is definitely stronger than the δ system under these conditions of excitation. It therefore seems that the transition $C\,^2\Sigma^+$ to $X\,^2\Pi$, corresponding to the δ system, may for some reason be partially forbidden, although the selection rules do not indicate this.

§6. CONCLUSION

It is quite certain, from the above discussion of the intensity distribution and from the examination of the $\Delta G'$ values, that the γ and ϵ bands of NO arise from separate electronic states and not, as suggested by Herzberg and Mundie, from normal and from predissociated vibrational levels of the same electronic state. Since the ϵ bands occur in emission from a source at relatively low gas-pressure, it follows also that the vibrational levels involved in the emission of the ϵ system are not predissociated.

Whether or not the levels of the γ system with $v'>3$ are predissociated remains unsettled. No band with $v'\geqslant 4$ has been observed, but this negative evidence is of little value because it so happens that all bands of the γ system with $v'\geqslant 4$ lie in regions of the spectrum which are strongly overlaid by more intense γ or ϵ bands. Since, however, vibrational levels of the C $^2\Sigma^+$ state (of the δ system) are known above the predicted positions for the $v'=4$ and 5 levels of the A $^2\Sigma^+$ state (of the γ system), these states being of similar type and not very different internuclear distance, there seems no reason to expect predissociation for the γ system.

It is uncertain whether the upper state of the ϵ system is $^2\Sigma^+$ or $^2\Sigma^-$, but in either case it seems difficult to reconcile the existence of a stable $^2\Sigma$ state with levels up to about 59985 cm.$^{-1}$ with a value for the dissociation energy as low as the accepted value of 5·29 ev. If the D state is $^2\Sigma^+$ then we have no fewer than three $^2\Sigma^+$ states lying above the normal dissociation products, $N(^4S)+O(^3P)$, the repulsive $^2\Sigma^+$ state from which should predissociate the observed $^2\Sigma^+$ states. If the D state is $^2\Sigma^-$, then we have the difficulty of explaining the existence of a stable vibrational level above the $^2\Sigma^-$ state resulting from the dissociation products $N(^4S)+O(^1D)$.

ACKNOWLEDGMENT

In conclusion, I wish to express my sincere thanks to Sir Alfred Egerton for his keen interest in these investigations, and to the Council of the Royal Society for financial assistance.

DESCRIPTION OF PLATE

(*a*) Spectrum of ordinary transformer discharge through air at low pressure. Small quartz spectrograph focused for 2000 A. region. Ilford Q.I. plate. Exposure 1 hr. Copper spark comparison spectrum.

(*b*) Transformer discharge. Small quartz focused for 2200 A. Q.II. plate. Exposure 5 min. Iron arc comparison.

(*c*) Transformer discharge. Small quartz. Q.II. plate. Exposure 2 min.

(*d*) Ozonizer-type discharge through nitrogen (containing a trace of oxygen) at atmospheric pressure. Q.II. plate. Exposure 1 hr.

(*e*) Transformer discharge. Medium quartz spectrograph. Zenith plate. Exposure 5 min.

(*f*) Ozonizer discharge. Medium quartz. Zenith plate. Exposure 1½ hr. Iron arc comparison.

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WIDE-APERTURE APLANATIC SINGLE LENSES

By L. C. MARTIN,

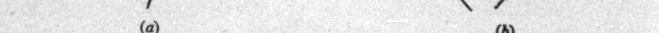
Technical Optics Section,

Imperial College of Science and Technology

ABSTRACT. This paper represents an essay in "Aspheric surface optics". Chrétien's theory of the aplanatic telescope suggests that the theory of aplanatic single lenses can be worked out on similar lines. The polar equation of an aspheric surface of such a lens is given in series form, and two numerical examples are studied, one of these being an aplanat, the other an anastigmatic singlet free from primary and higher-order spherical aberration, offence against the sine condition, primary astigmatism, and curvature of field. The shape of the latter lens is, however, predicted by Burch's "four-plate theorem", the results of which (as far as they concern primary aplanatism) are shown to agree with the formulae given in the paper.

§ 1. THEORY OF APLANATIC LENS

CHRÉTIEN'S theory of the aplanatic telescope (Chrétien, 1922) suggests that the theory of aplanatic single lenses can be worked out on similar lines. Figure 1 shows a ray diagram of the telescope, in which Chrétien's notation is used, and a corresponding diagram of the lens. The notation used for the latter problem is identical as far as possible, so that the formula for the reflection case can be recovered from the refraction case by putting μ (the refractive index) equal to -1. (See Appendix.)



(*a*) (*b*)

Figure 1.

In each case the paraxial focal length of the system is taken as unity. The origin of co-ordinates is taken at X', the principal focus of the system; and a ray parallel to the axis of the system, which coincides with the x axis of reference, is incident on the first surface at the point I, (x, y_1).* It meets the second surface at I' and proceeds to X'. In the telescope the distance between I and I' is l; the axial distance between M' and M is e. These will correspond to optical paths of positive sign. The final angle between the ray and the axis is u,

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* x is numerically positive to the left of the origin.

The angles of incidence and refraction at the first and second surfaces are i, r; i', r' respectively (all positive). Then the fundamental conditions of aplanatism (as usually defined) are expressed in the lens case by the equations

(for axial path equality)

$$-x+\mu l+\rho=(\mu-1)e; \qquad \ldots\ldots(1)$$

(next for fulfilment of the sine condition, remembering the focal length is unity)

$$y_1=\sin u. \qquad \ldots\ldots(2)$$

The original ray will be parallel to the axis if

$$u-r'+i'+r-i=0. \qquad \ldots\ldots(3)$$

Geometry gives

$$x=\rho\cos u+l\cos(i-r), \qquad \ldots\ldots(4)$$

$$y_1=\rho\sin u+l\sin(i-r). \qquad \ldots\ldots(5)$$

The law of refraction gives

$$\sin i=\mu\sin r, \qquad \ldots\ldots(6a)$$

$$\sin r'=\mu\sin i'. \qquad \ldots\ldots(6b)$$

This completes the equations of condition. Following Chrétien, the polar equation of the second surface with respect to the origin X′ will be written

$$\rho=f(u), \qquad \ldots\ldots(7)$$

so that

$$\tan r'=\frac{1}{\rho}\frac{d\rho}{du}. \qquad \ldots\ldots(7a)$$

It is necessary to eliminate x, y_1, l, r', i', r and i, leaving a relation between ρ and u in which the following quantities may enter as constants: ρ_0 (i.e. the value of ρ for $u=0$), e and μ.

Following Chrétien, eliminate i and y_1 from (5) with the aid of (3) and (2):

$$\sin u=\rho\sin u-l\sin(r'-i'-u). \qquad \ldots\ldots(8)$$

Combine (1), (4) and (3), giving

$$(\mu-1)e=\rho(1-\cos u)+l\{\mu-\cos(r'-i'-u)\}. \qquad \ldots\ldots(9)$$

Eliminate l between (8) and (9), giving

$$(\mu-1)e=\rho(1-\cos u)-(1-\rho)\sin u\left[\frac{\mu-\cos(r'-i'-u)}{\sin(r'-i'-u)}\right]. \qquad \ldots\ldots(9a)$$

A solution will be possible if i' can be eliminated between equations (9*a*) and (6*b*), and the result of this used with (7*a*) to eliminate r'; but the expressions are more complex than in Chrétien's formulae, and the same methods cannot be applied.

Re-write (9*a*)

$$\begin{aligned}\mu[\rho-1]\sin u &= \sin\xi[(\mu-1)e\cos u-\sin^2 u+\rho(1-\cos u)]\\ &\quad -\cos\xi[(\mu-1)e\sin u+\sin u\cos u-\rho\sin u]. \qquad \ldots\ldots(10)\end{aligned}$$

where

$$\xi=r'-i', \qquad \ldots\ldots(11)$$

Let $\tan r' = t$,

hen $$\sin\xi = \frac{t}{1+t^2}\left[\left\{1+\left(1-\frac{1}{\mu^2}\right)t^2\right\}^{\frac{1}{2}} - \frac{1}{\mu}\right] \qquad \ldots\ldots(12)$$

and $$\cos\xi = \frac{1}{1+t^2}\left[\left\{1+\left(1-\frac{1}{\mu^2}\right)t^2\right\}^{\frac{1}{2}} + \frac{t^2}{\mu}\right]. \qquad \ldots\ldots(13)$$

If a series expression is assumed for equation (7), i.e.

$$\rho = \rho_0[1 + a_2u^2 + a_4u^4 + a_6u^6 + \text{ etc.}], \qquad \ldots\ldots(14)$$

we can find the corresponding coefficients of the powers of u in the expansion

$$t = \tan r' = \frac{1}{\rho}\frac{d\rho}{du} = b_1u + b_3u^3 + b_5u^5 + \text{ etc.} \qquad \ldots\ldots(15)$$

There remains only a somewhat lengthy algebraical process in order to expand both sides of equation (10) as series, in powers of u, in which the desired eliminations have been completed. By equating successive coefficients it is then possible to find explicit values * for a_2, a_4, a_6 etc., although the amount of work involved in determining them rapidly increases with the order of the term, and the calculation has not been carried beyond a_6. The following results appear:—

$$a_2 = \frac{\rho_0 + e - 1}{2\left(1-\frac{1}{\mu}\right)e}; \qquad \ldots\ldots(16)$$

$$a_4 = \frac{(\rho_0+e-1)^3\mu(\mu+1)}{8e^3(\mu-1)^2} + \frac{(\rho_0+e-1)^2\mu}{8(\mu-1)e^2}$$
$$+ \frac{(\rho_0+e-1)\mu\{(1-\mu)e+3(\mu+1)\}}{24(\mu-1)^2e^2} - \frac{\mu}{8(\mu-1)^2e}; \qquad \ldots\ldots(17$$

$$a_6 = -\frac{a_2\{(2\mu-1)\rho_0+8+(\mu-1)e\}}{72(\mu-1)e} - \frac{a_2{}^2}{6e}\left\{\frac{\rho_0-4+e(2\mu+1)}{3\mu} + \frac{2}{(\mu-1)}\right\} - \frac{a_2{}^3}{3\mu}$$
$$+ \frac{a_2{}^4}{3\mu e}\left[\left(\frac{\mu+1}{\mu}\right)^2\{(1-\mu)e-1+\rho_0\} + 4(1-\rho_0) - 2(\mu-1)e\right]$$
$$+ \frac{a_2{}^5}{3}\left[2\left(\frac{\mu-1}{\mu}\right)\left\{\left(\frac{\mu+1}{\mu}\right)^2-4\right\}\right] - \frac{a_4}{6(\mu-1)e}\{\rho_0(2-\mu)-4-2(\mu-1)e\}$$
$$+ a_2a_4\left[1+\frac{4}{3\mu e}\{\rho_0-1-(\mu-1)e\}\right] + \frac{4a_2{}^2a_4(\mu-1)}{\mu}$$
$$+ \frac{\mu}{720(\mu-1)^2e}\{(\mu-1)(\rho_0+e)-\mu+16\}. \qquad \ldots\ldots(18)$$

Checks on the accuracy of the expressions for a_2 and a_4 appear in the work below. In the case of a_6, a further check was obtained as follows The numerical

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* A calculation on the above lines was first carried out in 1935 by Dr. C. R. Burch and shown to the present writer, who had occasion to design a singlet aplanat during the winter of 1940–41. The calculation was therefore revised and extended for the purpose as far as the determination of a_6. References are made in the literature to a paper by Linnemann (1905) which the present writer has not been able to consult, but according to Gleichen the formulae developed therein are applied to lenses of apertures up to f/2.

value of this coefficient was calculated for the lens cited in the second example below, using the formulae just given; then if we express (10) in the form

$$A = B\sin\xi + C\cos\xi, \qquad \ldots\ldots(19)$$

it is possible to express A, B, C, $\sin\xi$ and $\cos\xi$ all as power series in u, and if we use the proper values of a_2 and a_4 a check numerical equation for a_6 is obtained by equating the coefficients of u^5 on the two sides of the expression (19). Additional checks have been obtained by working out optical path differences, etc., in cases where values of a_6, other than that suggested by the formula, have been assumed. See also *Note regarding Chrétien's formula* at the end of this paper.

§ 2. NUMERICAL EXAMPLE I (DOUBLE CONVEX APLANAT)

The following values were assumed for the first calculation:

$$\mu = 1{\cdot}5, \qquad \rho_0 = 0{\cdot}8, \qquad e = 0{\cdot}4$$

(remember that the focal length was assumed to be unity); then calculation of the coefficients gave

$$a_2 = 0{\cdot}750, \qquad a_4 = 0{\cdot}734, \qquad a_6 = 1{\cdot}725.$$

The next step was to calculate, for various values of u, the corresponding values of ρ which determine the shape of the back surface, supposing the series for ρ to contain the above terms only. A check on the aplanatism is then obtained, as follows. Using equation (7 a), the values of r' and i' are obtained numerically for each value of u, and hence the slope U of the ray (inside the lens), which is supposed to be traced backwards from the origin through the rear surface. If y_1 and y_2 are the heights of intersection of this ray in the front and rear surfaces respectively, we should have (if the sine condition is fulfilled, see equation (2) above)

$$y_1 = \sin u,$$

and since

$$y_2 = \rho \sin u,$$

$$y_1 - y_2 = (1-\rho)\sin u.$$

The length of the path inside the lens should then be

$$l = \frac{y_1 - y_2}{\sin U},$$

and this value of l should result in fulfilling the optical-path equation,

$$-x + \mu l + \rho = (\mu - 1)e. \qquad \ldots\ldots(20)$$

For this we calculate

$$x = \rho\cos u + l\cos U$$

and obtain the following values for the left-hand side (L.H.S.) of (20), using six-figure logs:

u (radians)	0·0	0·1	0·15	0·2	0·25
L.H.S.	0·2000	0·1997	0·1999	0·1996	0·1990

The calculation for 0·1 radian is somewhat subject to numerical inaccuracy, but the agreement indicates that if the ray path fulfils the sine condition it will then (very nearly) fulfil the condition of constant optical length. The aperture reached for 0·25 radian is nearly f/2. However, the use of a series with only four terms can hardly be expected to give results which are adequate for such a large aperture.

The tendency appears to be for the successive coefficients of u to increase, so that the convergency of the series for ρ is weak, and this is especially the case for the series for r'. A drawing suggested that a term in u^8 (actually $9{\cdot}52u^8$ was tried) might improve matters. Taking $u=0{\cdot}25$ radian, the L.H.S. came to 0·2006, the correction now being overdone; a nearer approach was made with terms of $4{\cdot}71u^8$ and $75u^{10}$. The series is now

$$\rho=0{\cdot}8[1+0{\cdot}75u^2+0{\cdot}734u^4+1{\cdot}725u^6+4{\cdot}71u^8+75u^{10}].$$

The shape is suggested in figure 2. Graphical trials showed that the form of the aplanatic lens would be such as to find its limiting aperture when the refracted ray has grazing emergence; this would mean an infinite value for tan r', and the series would have to be divergent; series of the above type are not applicable.

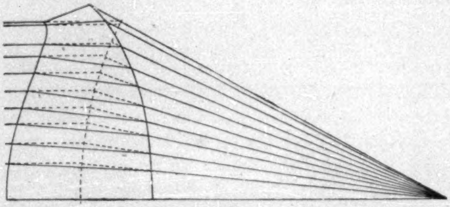

Figure 2. Aplanatic lens.

Numerical trials for the form suggested above were made by calculating the path length l inside the lens which would yield a constancy of optical path (complete elimination of spherical aberration); hence the value of y_1 and the corresponding offence against the sine condition (OSC) were calculated.

u	0·25 rad.	17°	20°	22°·5	25°
l	0·3433	0·3200	0·2883	0·2550	0·2185
OSC	0·00064	0·0064	0·0050	−0·0103	+0·0068

It appears that only a rough approximation to the shape of the truly aplanatic lens has been found for the larger angles, but the ideal shape will probably not be very different from the above. In comparison with the above, semi-aplanatic lenses can be designed with one spherical and one aspherical surface which can be given very high apertures, up to $u=35°$, without an offence against the sine condition exceeding $\pm 0{\cdot}014$. Within its limitations, however, the lens described above has the aberration under better control.

§3. NUMERICAL EXAMPLE II (ANASTIGMATIC SINGLET)

A recent paper by Burch (1943) has given formulae, based on the "see-saw diagram", for the design of anastigmatic singlet lenses. The notation used is as follows:—

Radius of first surface $= p$ Thickness of lens $= d$
,, ,, ,, $= R$ Refractive index $= n$

In order to secure a zero Petzval sum, $R=p$; and it is shown in the theory that there are in general two solutions for a value of d/p which will make the singlet lens aplanatic and anastigmatic, as far as the primary aberrations are concerned, for an object plane at an infinite distance. In particular there is a critical value of n, viz. 1·602, for which the two solutions coincide, and this is the lowest refractive index for which a solution is possible. In this case it is shown,

$$\frac{d}{p}=\frac{n+1}{2n(n-1)}=1\cdot34902.$$

It was thought to be of some interest to compare the predictions of this theory with that set out in the earlier part of the present paper, since the anastigmat should be aplanatic into the bargain. First the radii and thickness are calculated for a lens of unit focal length. Writing F_1 and F_2 for the powers of the two surfaces,

$$F_1=0\cdot602/p \quad \text{and} \quad F_2=-0\cdot602/p,$$

and putting the power F of the whole system equal to unity, i.e.

$$F=1=F_1+F_2-F_1F_2\,d/n,$$

we find
$$R=p=0\cdot30517$$
and
$$d=0\cdot41167.$$

A paraxial ray trace gives the position of the intermediate image (distance from pole of first surface $=l_1'$) as

$$l_1'=0\cdot81210$$

and of the final image (distance from pole of second surface $=l_2'$) as

$$l_2'=0\cdot49307.$$

The four-plate theorem of the paper by Burch allows the necessary "figuring" to be calculated for each surface, the actual amounts (the glass thickness to be added in each case) being

$$\text{“}R\text{” figuring}=18\cdot12\,h^4,$$
$$\text{“}p\text{” figuring}=0\cdot653\,h^4,$$

where h is the distance from the axis.

Given the thickness and the image distance from the second surface, the analytical formulae given in the early part of this paper allow the figure of the second surface to be calculated independently, as given by the polar equation

$$\rho=\rho_0[1+a_2u^2+a_4u^4+a_6u^6+\text{ etc.}].$$

Putting in the required values in the formula for a_2, etc., i.e.

$$\mu=1{\cdot}602, \quad e=d=0{\cdot}41167, \quad \text{and} \quad \rho_0=l_2'=0{\cdot}49307,$$

we find

$$a_2=-0{\cdot}30789, \quad a_4=-2{\cdot}12401, \quad a_6=-6{\cdot}508.$$

Since from the above series the axial radius of curvature R of the second surface is

$$R=\frac{\rho_0}{1-2a_2}, \qquad \ldots\ldots(21)$$

and numerical computation gives the value of 0·30517, this checks the axial shape of the lens predicted by the four-plate theorem.

To estimate the primary figuring, i.e. the departure from a spherical surface, we require the polar equation of a circle of the above radius with respect to the same origin, i.e. the focus. Putting D for the distance of a point on the circle from this point (figure 3), we require the coefficients A and B in the equation

$$D=0{\cdot}49307+Au^2+Bu^4+\text{ etc.} \qquad \ldots\ldots(22)$$

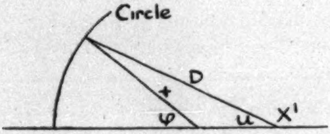

Figure 3.

Writing r for the radius of the circle, we have

$$D\sin u = r\sin\phi,$$
$$D\cos u = r\cos\phi+\rho_0-r,$$

where ϕ is the angle between the radius vector and the axis. In this case

$$D\sin u \qquad\qquad =0{\cdot}30517\sin\phi,$$
$$D\cos u-0{\cdot}18790=0{\cdot}30517\cos\phi,$$

whence, on squaring and adding,

$$D^2-0{\cdot}37580\,D\cos u+(0{\cdot}18790)^2-(0{\cdot}30517)^2=0.$$

Expanding in powers of u, and equating the coefficients of successive terms to zero, we get the values of A and B in (22), and hence the polar equation of the circle, in the form

$$D=0{\cdot}49307-0{\cdot}15183u^2+0{\cdot}02162u^4+\text{ etc.}$$

The corresponding equation of the aspheric surface being

$$D=0{\cdot}49307-0{\cdot}15183u^2-1{\cdot}0473u^4-3{\cdot}209u^6-\text{etc.}, \qquad \ldots\ldots(23)$$

it is seen that the thickness of glass to be added is $1{\cdot}0689u^4$. The thickness predicted by the four-plate theorem is

$$18{\cdot}12h^4=18{\cdot}12(0{\cdot}49307)^4u^4\,(\text{approx.})=1{\cdot}071u^4.$$

This seems a satisfactory check in view of the inaccuracies which may arise in rather long numerical work.

Check on aplanatism of the second lens. The aplanatism of this second lens was checked in exactly the same way as the first, i.e. by assuming the fulfilment of the optical sine condition and calculating the relative optical paths. Referring to equation (20), the relative values of the left-hand side (L.H.S.) for a number of values of *u* were computed as follows:—

u (radians)	0·0	0·1	0·15	0·2	0·25
L.H.S.	0·24784	0·24790	0·24800	0·24849	0·25148
(Amended: see below)	0·24784		0·24766		0·24797

The residual errors in L.H.S. are consistent with the probable effect of the missing term in u^8 and higher. In searching for likely values of these, numerical trials led to the following series as a compromise:

$$\rho=0\cdot4931(1-0\cdot30789u^2-2\cdot1240u^4-6\cdot712u^6-51u^8), \qquad \ldots\ldots(24)$$

from which the "amended" values were calculated. The lens is thus, of course, still imperfect, but it should be approaching the shape in which it is free from spherical aberration of the first few orders, from offence against the sine condition, and from primary astigmatism. Without going into further efforts to secure the exact formula on paper it was considered of some interest to submit the design to ray-tracing. For this purpose a few methods were examined, and they have been described in a contribution to a discussion (Martin, 1943). In figure 4 the two surfaces of the lens have been extended somewhat further by graphical trials.

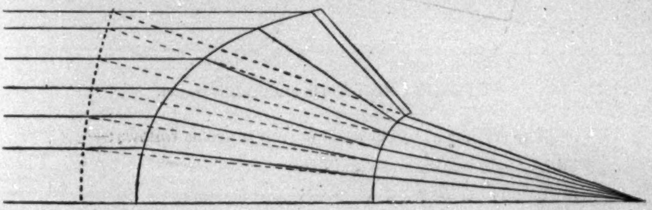

Figure 4.

In the first place, however, the exact value of the figuring to be assumed for the first surface must be settled. The value derived from the four-plate theorem is based on primary spherical aberration only; in practice it would be better to modify the numerical coefficient so as to obtain a compromise "h^4" figuring which would be suitable for a ray having a final u of medium amount; the ray $u=0\cdot15$ rad. was, therefore, traced backwards; it should emerge with a height$=0\cdot149437$. If the figuring (f) of the original estimate ($f=0\cdot653h^4$) is correct, the inclination between the surface and the arc of the "0·3052" circle at that height is

$$\frac{df}{dh}=2\cdot6133h^3=0\cdot00872 \text{ radian.}$$

The ray can thus be traced out into air; it is found to be converging towards the axis by about 59″. A few numerical trials showed, however, that a figuring of $0{\cdot}683h^4$ would bring it out practically parallel to the axis. This value was assumed for the front surface as a whole, the back surface being represented by (24).

§4. RESULTS OF RAY TRACING

Results may be quoted for anastigmatic fans in connection with two rays, nos. 1 and 3, incident at the pole of the first surface; also for a group of three rays (2, 3, 4) parallel to each other in the object space. (See figure 5.)

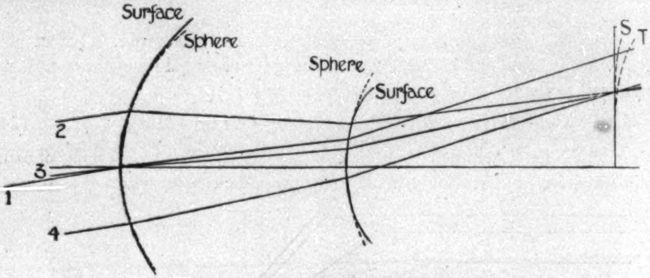

Figure 5. Ray traces in anastigmatic singlet.

The symbols employed to express the results are as follows:—

U_1	initial angle between ray and axis;
U_2'	final angle between ray and axis;
s_2', t_2'	distances of sagittal and tangential foci from last surface;
D_s, D_t	distances of sagittal and tangential foci from axial focal plane;
H	intersection height of ray in axial focal plane.

Astigmatic fan (object distance: infinity):—

Ray	U_1	y_1	y_2	U_2'	s_2'	t_2'	D_s	D_t
1	−10° 49′ 20″	0	0·0491	−17° 17′ 56″	0·5176	0·5428	0·007	0·032
3	− 7° 30′ 0″	0	0·0338	−11° 36′ 12″	0·502	0·507	0·000	0·005

Ray	U_1	y_1	y_2	U_2'	H
2	−7° 30′ 0″	0·1	0·0801	− 6° 40′ 15″	0·13649
3	−7° 30′ 0″	0·0	0·0338	−11° 36′ 12″	0·13469
4	−7° 30′ 0″	−0·1	0·0171	−17° 6′ 0″	0·13447

The correction of coma, astigmatism and field curvature is thus seen to be reasonably good over a semi-field of about 7° 30′, when the lens works at f/5. Beyond this, the higher-order terms in coma and astigmatism represent a rapid deterioration. The spherical correction is, of course, practically complete up to large aperture, but the fulfilment of the sine condition eliminates only those terms in the coma expression which depend on even powers of the zonal radius and the first power of the image height. It may be worth recalling that, as far as the primary aberrations are concerned, the anastigmatic correction is now independent of the stop position.

APPENDIX

Note on comparison with Chrétien's formula

Chrétien gives the following formula representing (in his notation) the polar equation of the small mirror:—

$$\frac{\rho}{m} = 1 + \left(1 + \frac{1-m}{e}\right) t + \left\{\left(1 + \frac{1-m}{e}\right)^2 - \frac{1}{2e}\right\} t^2$$
$$+ \left\{\left(1 + \frac{1-m}{e}\right)^3 - \frac{1}{e}\left(1 + \frac{1-m}{e}\right) - \frac{1+e}{6e^2}\right\} t^3 + \text{etc.},$$

where m is the distance of the focus from the apex (ρ_0 in the present paper) and

$$t = \sin^2(u/2).$$

Putting

$$\sin\frac{u}{2} = \frac{u}{2} - \frac{(u/2)^3}{3!} + \frac{(u/2)^5}{5!} - \text{etc.},$$

we readily find

$$\frac{\rho}{m} = 1 + \frac{u^2}{4}\left(1 + \frac{1-m}{e}\right) + u^4\left[\frac{1}{16}\left\{\left(1 + \frac{1-m}{e}\right)^2 - \frac{1}{2e}\right\} - \frac{1}{48}\left(1 + \frac{1-m}{e}\right)\right]$$
$$+ u^6\left[\frac{1}{64}\left\{\left(1 + \frac{1-m}{e}\right)^3 - \frac{1}{e}\left(1 + \frac{1-m}{e}\right) - \frac{1+e}{6e^2}\right\} - \frac{1}{96}\left\{\left(1 + \frac{1-m}{e}\right)^2 - \frac{1}{2e}\right\}\right.$$
$$\left. + \frac{1}{1440}\left(1 + \frac{1-m}{e}\right)\right] + \text{etc.},$$

or

$$\frac{\rho}{m} = 1 + a_2^{\bullet} u^2 + a_4^{\bullet} u^4 + a_6^{\bullet} u^6 + \text{etc.},$$

where

$$a_2^{\bullet} = \frac{1+e-m}{4e},$$

$$a_4^{\bullet} = a_2^{\bullet 2} - \frac{a_2^{\bullet}}{12} - \frac{1}{32e},$$

$$a_6^{\bullet} = a_2^{\bullet 3} - \frac{a_2^{\bullet 2}}{6} + a_2^{\bullet 2}\left\{\frac{1}{360} - \frac{1}{16e}\right\} + \frac{1}{384}\left(\frac{e-1}{e^2}\right).$$

It involves only straightforward, though rather long, algebra to show that, on putting $\mu = -1$, and also substituting $-e$ for e (so as to make the optical path μe positive) in equations (16), (17) and (18) of the present paper, the values of the coefficients agree with those above, as they should. This constitutes an additional check on the accuracy of the expressions.

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TRACING SKEW RAYS THROUGH SECOND-DEGREE SURFACES

By Instructor-Captain T. Y. BAKER, F.Inst.P., R.N.,
Leicester

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The tracing of skew rays is necessarily a more laborious business than the tracing of rays which lie in a meridional plane, and many optical designers do not attempt the task, but hope that if they have designed the system so that a number of rays " in the plane " all cut the image plane in the right place all will be well. This is not theoretically justifiable, and at least one ray passing through " 3 o'clock " in the aperture stop should be traced through the system. The method is straightforward, but passage through each surface must be reckoned to require at least three times as long as for an ordinary ray.

The ray is most conveniently defined by the co-ordinates of some point through which it passes and its direction-cosines—that is to say, the cosines of the angles which it makes with the axes of reference. In the work which follows, these axes, of which Ox lies along the optical axis, are shifted from surface to surface as they are successively dealt with. For the direction-cosines I prefer to use $\cos\theta$, $\sin\theta\sin\phi$, $\sin\theta\cos\phi$, so that θ is the angle that the ray makes with Ox and ϕ the angle between the plane containing the direction of the ray and Ox and the plane xOy. The point on the ray to which reference has been made is usually the point of intersection with the previous surface with the x-co-ordinate modified to take account of the shift of axes from one surface to the next. The θ and ϕ remain unaltered during this shift.

The process of computation involves

(1) determination of co-ordinates of the point where the ray cuts the surface;

(2) determination of the direction-cosines of the normal to the surface at this point;

(3) the refraction equation;

(4) determination of the direction-cosines of the refracted ray.

If the surface is spherical (2) is shortened; in fact for spherical surfaces one can evolve a trigonometrical technique which avoids all mention of direction-cosines or of the equations of the rays and surfaces. With non-spherical surfaces I do not think either point can be avoided, and since the numerical work is not appreciably longer than the trigonometrical trace of skew rays when the surface is spherical, I prefer to have one scheme that will cover all cases.

Let α, β, γ be a point on the ray and θ, ϕ its direction. Then for all points along the ray

$$(x-\alpha)/\cos\theta=(y-\beta)/\sin\theta\sin\phi=(z-\gamma)/\sin\theta\cos\phi. \quad \ldots\ldots(1)$$

The equation of the surface is

$$y^2+z^2=2rx-px^2. \qquad \ldots\ldots(2)$$

From (1) we obtain

$$y=\beta+\tan\theta\sin\phi(x-\alpha)$$

and

$$z=\gamma+\tan\theta\cos\phi(x-\alpha).$$

Substituting in (2), we obtain

$$x^2(p+\tan^2\theta)-2x\{r+\tan\theta(\alpha\tan\theta-\beta\sin\phi-\gamma\cos\phi)\}$$
$$+\alpha^2\tan^2\theta+\beta^2+\gamma^2-2\alpha\tan\theta(\beta\sin\phi+\gamma\cos\phi)=0,$$

or

$$x^2(p+\tan^2\theta)-2x\{r+\tan\theta(\alpha\tan\theta-\beta\sin\phi-\gamma\cos\phi)\}$$
$$+(\alpha\tan\theta-\beta\sin\phi-\gamma\cos\phi)^2+(\beta\cos\phi-\gamma\sin\phi)^2=0. \qquad \ldots\ldots(3)$$

The coefficients of x^2 and $-2x$ and the constant term have to be numerically evaluated, and the form (3) of the equation is one which, in my opinion, is the most suitable for logarithmic computation. It will be observed that the logarithms required in $\beta\cos\phi-\gamma\sin\phi$ have already been used in

$$\alpha\tan\theta-\beta\sin\phi-\gamma\cos\phi,$$

which expression occurs twice in the calculation.

Take, as an example, $\alpha=-25{\cdot}702$, $\beta=14{\cdot}710$, $\gamma=3{\cdot}146$, $\theta=9^\circ\,14'\,26''$, $\phi=27^\circ\,18'\,14''$, $p=-4{\cdot}27$ and $r=123{\cdot}0$

$\log(-\alpha)$	1·409967	$\log\beta$	1·167613	$\log\gamma$	0·497759		
$\log\tan\theta$	9·211364	$\log\sin\phi$	9·661538	$\log\cos\phi$	9·948700		
	0·621331		0·829151		0·446459		
$\log\tan^2\theta$	8·422728	$\log\beta\cos\phi$	1·116313	$\beta\cos\phi$	13·0711		
$\tan^2\theta$	0·02647	$\log\gamma\sin\phi$	0·159297	$\gamma\sin\phi$	1·4431		
p	−4·27						
				Diff	11·6280	log Diff	1·065505
	−4·24353						
		$\alpha\tan\theta$	−4·1815	$(\text{Diff})^2$	135·210		2·131010
$\log\tan\theta$	9·211364	$-\beta\sin\phi$	−6·7476			log Sum	1·137500
log Sum	1·137500	$-\gamma\cos\phi$	−2·7955				
−2·233	0·348864	Sum	−13·5246	$(\text{Sum})^2$	188·365		2·275000
123·000							
					323·575		
120·767							

The quadratic equation is, therefore,

$$-4{\cdot}24353x^2-2x\times120{\cdot}767+323{\cdot}575=0.$$

The method that I use of solving this quadratic is one depending on a certain set of logarithmic tables which need a little explanation.* The smaller root of the equation $ax^2-2bx+c=0$ is $(b-\sqrt{b^2-ac})/a$ or $(b/a)(1-\sqrt{1-ac/b^2})$. If ac/b^2 is called X and a table of $\log(1-\sqrt{1-X})$, tabulated in terms of $\log X$, is available, then a great deal of time can be saved in looking out logarithms. I have now tabulated this function for values of $\log X$, when X is positive, lying between $\bar{2}{\cdot}700$ and 0, giving a range of values of X from 0·0512 to unity (above which the roots are imaginary). For negative values of X the value of $\log(\sqrt{1-X}-1)$ in terms of $\log(-X)$ is tabulated from $\log(-X)=\bar{2}{\cdot}700$ to $\log(-X)=1{\cdot}000$, i.e. values of X from $-0{\cdot}0512$ to $-10{\cdot}000$. For numerically smaller values of X than 0·0512 an approximate method of solving the equation gives the required accuracy in the result very quickly. For instance, the equation $x^2-10x+1=0$ has a value for ac/b^2 of 0·04. The equation can be written $x=0{\cdot}1x^2+0{\cdot}1$. As a first approximation $x=0{\cdot}1$. Using this value in the right-hand side we get, as a closer approximation, $x=0{\cdot}101$. Now make use of this new value on the right-hand side and we obtain $x=0{\cdot}10102$, and any further approximation will not alter the first five figures.

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* See Appendix.

In the original equation there are four possible variations of sign among the three terms, since the last one can always be made positive, if necessary, by altering the signs of all three terms without affecting the values of the roots. The second term can be either positive or negative, but a change from one to the other is merely equivalent to a change in the sign of x without alteration of its magnitude. It will therefore be regarded always as a negative term (i.e. b positive), and where this is not the case the solution will have its sign changed. The practical possibilities thus reduce to two, viz., whether a is positive or negative, and these two correspond to the two parts of the table.

In using this table we write down first of all the logarithms of a, b and c. For the numerical equation we have found above these are

$$\begin{array}{llllll}
\log a & 0{\cdot}627727 & \log b & 2{\cdot}081948 & \log c & 2{\cdot}509975 \\
 & & \log b/a & 1{\cdot}454221 & \log c/b & 0{\cdot}428027 \\
 & & & \bar{2}{\cdot}662898 & \log ac/b^2 & \bar{2}{\cdot}973806 \\
\cline{4-4}
 & & & 0{\cdot}117119 & &
\end{array}$$

We get $\log b/a$ and $\log c/b$ by subtracting the first log from the second and the second from the third. Log ac/b^2 is obtained by subtracting these differences. Entering the negative table with the value $\bar{2}{\cdot}973806$, we obtain [*] from the table $\bar{2}{\cdot}666898$. Adding this to $\log b/a$, we find $\log x=0{\cdot}117119$ or $x=1{\cdot}3095$. If the other root of the equation were needed it could be found by subtracting the tabulated value from $\log c/b$.

We are now able to evaluate y and z.

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[*] The following is a short extract from this table:—

	0	1	2	3	4	5	6	7	8	9
$\bar{2}{\cdot}971$	$\bar{2}{\cdot}660152$	0250	0348	0446	0544	0641	0739	0837	0935	1033
·972	1131	1229	1327	1425	1523	1620	1718	1816	1914	2012
·973	2109	2207	2305	2403	2501	2598	2696	2794	2892	2990
·974	3087	3185	3283	3381	3479	3576	3674	3772	3870	3968
·975	4065	4163	4261	4359	4457	4554	4652	4750	4848	4946

$x-\alpha=27{\cdot}0115$	$\log(x-\alpha)$	1·431549		1·431549	$\log x$	0·117113
	$\log\tan\theta$	9·211364		9·211364	$\log p$	0·630428
	$\log\sin\phi$	9·661538	$\log\cos\phi$	0·948700		
		0·304451		0·591613		0·747541
	2·0158			3·9049		− 5·5917
β	14·710		γ	3·146		−123·0000
$y=$	16·7258		$z=$	7·0509		−128·5917

Thus the point of intersection is 1·3095, 16·7258, 7·0509. Included in the above figures is the calculation for $px-r$, which will be required, as shown in the succeeding paragraph, for the determination of the direction-cosines of the normal at the point.

The point where the ray cuts the surface has a normal lying in the direction for which the direction-cosines are proportional to $px-r$, y and z, that is to say, to $-128{\cdot}592$, $16{\cdot}726$, $7{\cdot}051$, or rather to $128{\cdot}592$, $-16{\cdot}726$, $-7{\cdot}051$, since it is a convenient convention to keep the x direction-cosine always positive. This statement applies to rays of light as well as to normals to refracting surfaces. Both will then be considered to make acute angles with the optical axis. If θ_G and ϕ_G are the corresponding values for the normal,

$$\sin\theta_G = \sqrt{(16{\cdot}726)^2+(7{\cdot}501)^2}/\sqrt{(128{\cdot}592)^2+(16{\cdot}726)^2+(7{\cdot}501)^2},$$
$$\tan\phi_G = 16{\cdot}726/7{\cdot}051.$$

The calculation work for these angles is below:

log 128·592	2·109214	log 16·726	1·223392	log 7·051	0·848251
16535·97	4·218428	279·76	2·446784	49·72	0·696502
329·48		49·72			
16865·45	4·226998	329·48	2·517829		
	2·113499		1·258914		
		$\log\sin\theta_G$	9·145415		
		$\log\tan\phi_G$	0·375141		

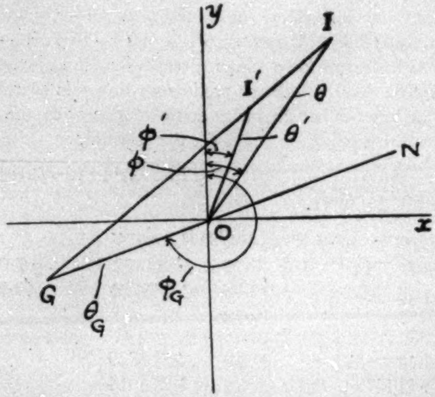
$$\theta_G = 8^\circ\ 2'\ 4''; \quad \phi_G = 67^\circ\ 8'\ 30'' \ \text{or}\ 247^\circ\ 8'\ 30''.$$

Some computers might prefer to use Barlow's Tables for the squares of the various quantities, but I have found that the interpolation necessary is troublesome and productive of errors.

If the computation had been in the meridian plane the angle of incidence would have been $\theta_G-\theta$, since the three *directions*, viz. incident ray, normal and optical axis, are co-planar. With a skew ray, however, these three directions are not co-planar, and it becomes necessary to solve a spherical triangle instead of doing a simple subtraction.

In doing this we are concerned only with the directions of the ray, the normal and the optical axis, and it is convenient to look at these directions as radiating from the centre of a sphere at which the eye is placed. The three directions cut the sphere in three points, forming a spherical triangle which has to be solved. In order to make the diagram easier to draw, think of these three directions extended beyond the surface of the sphere as far as the tangent plane at the point where the optical axis cuts the sphere. The spherical triangle will now be represented by a *plane* triangle which, however, has not the same angles as the spherical triangle, nor are its sides drawn to any definite or uniform scale. But it is worth while constructing this triangle with reasonable accuracy, since it enables a check to be kept on the trigonometry of the solution of the triangle, to "bowl out" any definite mistakes and to keep tally of the signs of the various values.

The whole scheme can best be appreciated from the numerical example that is being worked out. The point O represents the direction of the optical axis. The incident ray I is defined by $\phi = 27° 18' 14''$. If the radius of the sphere had been taken as unity, then the actual length of OI would have been $\tan\theta$, i.e. $\tan 9° 14' 26'' = 0{\cdot}1627$. The direction cosines are proportional to 128·592, −16·726, −7·051. The last two being both negative, the point G will lie in the south-west quadrant and OG is $\tan 8° 2' 4'' = 0{\cdot}1412$. The value of ϕ_G is 247° 8′ 30″, as shown in the diagram, and the angle yON is 67° 8′ 30″.



On the sphere the points I and G have to be joined by a great circle. This is represented in our diagram by a straight line IG, and the direction I′ of the refracted ray will be found in this line at a point where $n \sin \mathrm{GI} = n' \sin \mathrm{GI}'$. The solution of the spherical triangle therefore involves (*a*) determination of the angle GI and thence, from the refraction equation, the angle GI′ and (*b*) the determination of the angles OI′ and yOI′, which give the direction cosines of the refracted ray.

In order to carry out the numerical solution we need the values of the refractive indices, and these we will take to be $n = 1$ and $n' = 1{\cdot}5180$.

The evaluation of θ', ϕ', which determine the direction-cosines of the refracted ray, I′, requires the use of two standard spherical-triangle forumlae. In any spherical triangle in which the sides are a, b, c and the angles A, B, C, one standard relationship is $\sin a/\sin A = \sin b/\sin B = \sin c/\sin C$. These equations are suitable for logarithmic computation. The second standard formula gives the cosine of one side when the other two sides and the angle between them are known. One such formula for the determination of a when b, c, A are known is

$$\cos a = \cos b \cos c + \sin b \sin c \cos A.$$

This formula is not suitable for logarithmic computation, and it should be noted here that the evaluation of an angle from its cosine or its log cosine is not desirable if accuracy is necessary and the angle is likely to be below 25°. Using six-figure logarithms, a variation of 1″ in the angle corresponds to a variation of one unit in the sixth place when the angle is 25°. For smaller angles, if 1″ accuracy is required six-figure tables are inadequate. If, however, the computation formulae are modified so that the angles are derived from their log sines rather than from their log cosines, then six-figure tables are good enough for angles up to about 60°. It is this question of accuracy that makes it preferable to compute θ_g from its sine rather than from the more obvious formula for the cosine.

The standard cosine formula is modified as follows:

$$\begin{aligned}\cos a &= \cos b \cos c\,(\cos^2 \tfrac{1}{2}A + \sin^2 \tfrac{1}{2}A) + \sin b \sin c\,(\cos^2 \tfrac{1}{2}A - \sin^2 \tfrac{1}{2}A)\\ &= \cos (b-c) \cos^2 \tfrac{1}{2}A + \cos (b+c) \sin^2 \tfrac{1}{2}A,\end{aligned}$$

whence

$$\sin^2 \tfrac{1}{2}a = \sin^2 \tfrac{1}{2}(b-c) \cos^2 \tfrac{1}{2}A + \sin^2 \tfrac{1}{2}(b+c) \sin^2 \tfrac{1}{2}A.$$

Used in this form, the standard cosine formula is easy to work numerically. All terms are positive and no sign convention is needed.

The exact way in which the numerical work is put down lies with the individual, but one or two tips that I, personally, have found economical in the amount of figures to be written down may be of interest to others. In computing $\tfrac{1}{2}(b+c)$, which is the mean between b and c, both positive angles, I find it a very simple matter to write down the answer direct from left to right without adding the two angles and dividing by two. It requires a little practice to acquire this habit, but it is well worth the effort. Having obtained $\tfrac{1}{2}(b+c)$ in this manner, $\tfrac{1}{2}(b-c)$ is found by subtracting the smaller angle.

Another tip is to write down $\log \sin^2 \tfrac{1}{2}(b-c)$, etc., directly from the table of log sines, doubling the values as one takes them out. If one has a table of log sines to seconds there is no difficulty, though interpolation requires care.

A third tip in connection with this formula is that we obtain a numerical value for $\sin^2 \tfrac{1}{2}a$. By subtracting this from unity we obtain $\cos^2 \tfrac{1}{2}a$. If we take out the logarithms of these two numbers and put down the mean of the two logarithms we get $\log(\sin \tfrac{1}{2}a \cos \tfrac{1}{2}a)$; adding 0·301030, we get $\log \sin a$, which we need in the refraction equation, and a itself need not be looked out.

The angle GOI has to be calculated from the known directions of ON, OG and OI. I prefer to have no sign convention for this kind of computation, but to rely on a diagram and common sense.

The sequence of operations for the determination of the direction of the emergent ray is as follows: (1) find the log sin GI by the cosine formula as detailed above; (2) find G from the sine formula sin G = sin GOI sin OI/sin GI; (3) determine GI′ from the refraction equation n sin GI = n' sin GI′; (4) find OI′ from the cosine equation using the two sides GO, GI′ and the included angle G; (5) find GOI′ from the sine formula sin GOI′ = sin G sin GI′/sin OI′; (6) determine ϕ, the angle yOI′.

The numerical work required for this computation is given below, without any further explanation. The figures are all that are needed in a numerical computation. The reader should have no difficulty in following them.

° ′ ″	° ′ ″			
67 8 30	9 14 26			
27 18 14	8 2 4			
39 50 16	8 38 15	$\bar{2}$·353238	0° 36′ 11″	$\bar{4}$·044454
140 9 44		$\bar{1}$·946419		$\bar{1}$·064764
70 4 52				
		$\bar{2}$·299657	0·01993686	$\bar{5}$·109218
			0·00001286	
9·806598			0·01994972	$\bar{2}$·299937
9·205691			0·98005028	$\bar{1}$·991248
0·553378				
				$\bar{1}$·145592
9·565667	G 21 34 58			0·301030
	½G 10 47 29		log sin GI	9·446622
				0·181272
	10 36 58		log sin GI′	9·265350
	8 2 4			
	9 19 31	$\bar{2}$·419240	1° 17′ 27″	$\bar{4}$·705422
		$\bar{2}$·544768		$\bar{1}$·984501
		$\bar{4}$·964008	0·000920466	$\bar{4}$·689923
			0·000489692	
9·565667			0·001410158	$\bar{3}$·149268
9·265350			0·998589842	$\bar{1}$·999387
1·124643				$\bar{2}$·574327
				0·301030
9·955660	115 27 8			
	67 8 30		log sin OI′	8·875357
	182 35 38			

$\phi' = 2^\circ\ 35'\ 38''$ $\qquad$ $\theta' = 4^\circ\ 18'\ 15''$

This completes the calculation except for the transference of co-ordinates to the new set of axes. We started with a ray through −25·702, 14·710, 3·146 in direction (θ, ϕ) 9° 14′ 26″, 27° 18′ 14″ to meet the non-spherical surface

$p=-4{\cdot}27$, $r=123{\cdot}0$, and find that it cuts the surface at 1·3095, 16·7258, 7·0509, and that the refracted ray, if the initial refractive index is 1 and the final 1·5180, has direction 4° 18′ 15″, 2° 35′ 38″.

There is no hope of tracing skew rays at anything like the speed with which "in the plane" rays can be traced. The beginner will find that one per hour is not bad. When he is expert he might halve that time.

It is not necessary to trace nearly as many skew rays as plane rays. One refractive index is usually sufficient, and the ray which cuts the aperture stop at "3 o'clock" should be chosen, using something between the full aperture and 0·8 of the full aperture. A skew ray with these characteristics should be traced for at least two positions in the field, say at full field and 0·7 of full field.

In cases of photographic lenses, where the actual stop is inside the lens, the position of the image of this stop in the object space should be calculated by paraxial equations and the ray-trace started from this virtual stop.

APPENDIX

Tables for solving quadratic equations

The equation $ax^2-2bx+c=0$ has roots $(b\pm\sqrt{b^2-ac})/a$ or $(b/a)(1\pm\sqrt{1-ac/b^2})$. The log of the smaller root is $\log(b/a)+\log(1-\sqrt{1-X})$, where X stands for ac/b^2. The log of the larger root is $\log(c/b)-\log(1-\sqrt{1-X})$.

In these tables $\log(1-\sqrt{1-X})$ is tabulated with $\log X$ as argument. The tables are in two parts, A and B corresponding to the cases of the roots being of the same or of opposite signs. If the coefficient a be made invariably positive, table A must be used when c is positive, table B when c is negative. If b is positive, both roots are positive in case A, and the larger root positive in case B. If b is negative, both roots are negative in case A, and the larger root negative in case B.

Owing to the difficulties of getting new tables published at the present time, it has been suggested that a skeleton table would enable anyone interested to fill in the gaps for himself. The number of entries necessary to cover the case of linear interpolation is too great, but from the following 92 entries the full tables of 13,000 entries in A and 23,000 in B can be compiled by "mean second difference" interpolation with an accuracy of about two units in the sixth place. As binary interpolation is much easier to carry out than a decimal subdivision when second and third differences are involved, the key entries are given at intervals of 64, 32, 16, 8, 4 or 2 units in the argument to ensure that in the first interpolation the error by the mean second-difference method shall not exceed two in the sixth place. For the last little bit of table A, where the roots are very nearly equal, this method of interpolation is no longer effective.

The following are the rules for "mean second-difference" interpolation:—Write down in a vertical column the key entries, leaving sufficient space for the intervening entries. In the next vertical column put down the differences between successive key entries in the first, taking care that each first difference is on a level half-way between the corresponding entries in the first column. Now, in a third vertical column, put down the second differences, i.e. differences of the first differences. These will be found to lie on the same levels as the key entries. In the second-difference column, half-way between the key entries, put down the mean of the second differences, one above and the other below. If one-eighth of this mean second difference is subtracted from the mean of the two key entries it will give the correct tabular entry for the first column and should be written down there. In this way the first binary subdivision is carried out. For the next " middling", as the process is called, the mean second difference is first put down in the third column, whilst in column 1 is entered the mean of the entries above and below, less 1/32nd of that entry, which lies on the same level in the third column. The third middling involves the subtraction of 1/128th part of the third-column entry. Successive fractions are each one-quarter of the preceding one, and one quickly reaches the stage where the second-difference correction is negligible. An extension of column 1 across the page for decimal subdivision of the argument is in all cases a linear interpolation.

Skeleton for table A

To be used when the roots are of the same sign

$\bar{2}$·636	$\bar{2}$·339745	$\bar{1}$·436	$\bar{1}$·168194	$\bar{1}$·908	$\bar{1}$·750566
$\bar{2}$·700	$\bar{2}$·404516	$\bar{1}$·468	$\bar{1}$·203093	$\bar{1}$·916	$\bar{1}$·763908
$\bar{2}$·764	$\bar{2}$·469417	$\bar{1}$·500	$\bar{1}$·238284	$\bar{1}$·924	$\bar{1}$·777663
$\bar{2}$·828	$\bar{2}$·534468	$\bar{1}$·532	$\bar{1}$·273805	$\bar{1}$·932	$\bar{1}$·791901
$\bar{2}$·892	$\bar{2}$·599697	$\bar{1}$·564	$\bar{1}$·309702	$\bar{1}$·940	$\bar{1}$·806712
$\bar{2}$·956	$\bar{2}$·665132	$\bar{1}$·596	$\bar{1}$·346028	$\bar{1}$·948	$\bar{1}$·822218
$\bar{1}$·020	$\bar{2}$·730814	$\bar{1}$·628	$\bar{1}$·382849	$\bar{1}$·956	$\bar{1}$·838595
$\bar{1}$·084	$\bar{2}$·796787	$\bar{1}$·660	$\bar{1}$·420243		
$\bar{1}$·148	$\bar{2}$·863111	$\bar{1}$·692	$\bar{1}$·458316	$\bar{1}$·960	$\bar{1}$·847183
$\bar{1}$·212	$\bar{2}$·929851	$\bar{1}$·724	$\bar{1}$·497191	$\bar{1}$·964	$\bar{1}$·856096
$\bar{1}$·276	$\bar{2}$·997094			$\bar{1}$·968	$\bar{1}$·865386
$\bar{1}$·340	$\bar{1}$·064949	$\bar{1}$·756	$\bar{1}$·537040	$\bar{1}$·972	$\bar{1}$·875133
$\bar{1}$·404	$\bar{1}$·333556	$\bar{1}$·772	$\bar{1}$·557397	$\bar{1}$·976	$\bar{1}$·885437
		$\bar{1}$·788	$\bar{1}$·578088	$\bar{1}$·980	$\bar{1}$·896444
		$\bar{1}$·804	$\bar{1}$·599157		
		$\bar{1}$·820	$\bar{1}$·620656	$\bar{1}$·982	$\bar{1}$·902278
		$\bar{1}$·836	$\bar{1}$·642649	$\bar{1}$·984	$\bar{1}$·908386
		$\bar{1}$·852	$\bar{1}$·665216	$\bar{1}$·986	$\bar{1}$·914816
		$\bar{1}$·868	$\bar{1}$·688461	$\bar{1}$·988	$\bar{1}$·921643
		$\bar{1}$·884	$\bar{1}$·712521		
		$\bar{1}$·900	$\bar{1}$·737582		
				0·000	0·000000

Skeleton for table B

To be used when the roots are of opposite signs

$\bar{2}$·636	$\bar{2}$·330358	$\bar{1}$·532	$\bar{1}$·197997	0·364	$\bar{1}$·913765
$\bar{2}$·700	$\bar{2}$·393626	$\bar{1}$·596	$\bar{1}$·257370	0·428	$\bar{1}$·962897
$\bar{2}$·764	$\bar{2}$·456797	$\bar{1}$·660	$\bar{1}$·316176	0·492	0·011135
$\bar{2}$·828	$\bar{2}$·519841	$\bar{1}$·724	$\bar{1}$·374373	0·556	0·058493
$\bar{2}$·892	$\bar{2}$·582740	$\bar{1}$·788	$\bar{1}$·431909	0·620	0·104991
$\bar{2}$·956	$\bar{2}$·645475	$\bar{1}$·852	$\bar{1}$·488739	0·684	0·150652
$\bar{1}$·020	$\bar{2}$·708023	$\bar{1}$·916	$\bar{1}$·544820	0·748	0·195505
$\bar{1}$·084	$\bar{2}$·770358	$\bar{1}$·980	$\bar{1}$·600113	0·812	0·239579
$\bar{1}$·148	$\bar{2}$·832451	0·044	$\bar{1}$·654582	0·876	0·282907
$\bar{1}$·212	$\bar{2}$·894273	0·108	$\bar{1}$·708198	0·940	0·325522
$\bar{1}$·276	$\bar{2}$·955787	0·172	$\bar{1}$·760939	1·004	0·367458
$\bar{1}$·340	$\bar{1}$·016958	0·236	$\bar{1}$·812785	1·068	0·408749
$\bar{1}$·404	$\bar{1}$·077743	0·300	$\bar{1}$·863729	1·132	0·449447
$\bar{1}$·468	$\bar{1}$·138106				

The first key entry for $\bar{2}$·636 in both tables is included for the purpose of enabling the second difference to be calculated at the level $\bar{2}$·700, where the table really starts.

THE RECTIFYING PROPERTY OF CARBORUNDUM

By J. T. KENDALL,

Research Department, Metropolitan-Vickers Electrical Co., Ltd., Manchester

MS. received 26 *November* 1943

ABSTRACT. A technique is described for obtaining a non-rectifying carbon-carborundum contact. Experimental current-voltage curves are given for single rectifying contacts. These curves show that *green* and *black* carborundum are essentially different types of semi-conductor. Experiment also shows that all the rectification takes place at the contact surface, and that any volume rectification (if it exists) is a second-order effect.

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§1. INTRODUCTION

Much of the literature on the rectifying property of carborundum is confusing, owing to a lack of attention to two important factors. First, there are at least two types of carborundum crystals which are completely different in their electrical properties. In *green* carborundum, rectification takes place in such a way that the direction of easy flow of electrons is from semi-conductor to metal; in *black* or *blue* carborundum, rectification is in the opposite direction. This fact is evidently not generally appreciated, for as recently as 1942, Fairweather, in describing experiments on the carborundum rectifier, omits to mention with what type of crystal he is dealing. On the other hand, as early as 1921 Dowsett distinguished between *green* and *black* crystals, which he called positive and negative; and more recently Russian investigators (e.g. Gokhberg (1937) and Losev (1940)) have distinguished the two types as *excess* and *defect* semi-conductors. (See Wilson (1939) for an explanation of these terms.)

Commercial carborundum, as manufactured in the electric furnace, consists mainly of masses of opaque black or deep blue crystals, but in parts of the furnace the product may consist of clear crystals, varying in colour from green to pale yellow or even colourless. The various crystals differ little, if at all, in chemical composition. They may differ in crystal structure, and an investigation on this point is at present in progress.

Secondly, the fact that experimental data may refer to two contacts in series is often not mentioned. For example, El Sherbini and Yousef (1939, 1941), Khastgir and Das Gupta (1935), Chakravarty and Khastgir (1937), and others, clamp a crystal in metal electrodes and measure the *overall* rectification. If there is no volume rectification this simply gives the difference between the rectification at the two contacts, and the results can become very misleading. As shown below, even a soldered contact does not have under all conditions a resistance small compared with that of a cat's-whisker contact. Fairweather (1942) has avoided the difficulty, and has measured the voltage across a single

9-2

contact by a potential probe and balancing e.m.f. This method is theoretically sound, but is comparatively insensitive, especially for small voltages, owing to the high resistance of the measuring circuit.

In the present series of experiments full account has been taken of these two important factors. Data are presented for both green and black carborundum, and the rectification is referred to a single contact by making the resistance of the second contact very small.

The crystal fragments used were roughly rectangular, having a volume of about 0·01 c.c. There is an advantage in experimenting on such a small scale, for commercial carborundum is a mass of irregularly fractured crystals, and it is difficult to obtain a single crystal of larger size.

§2. METHOD OF MAKING A "LOW-RESISTANCE" CONTACT

Three types of low-resistance contact have been tried: solder, mercury and carbon. In the first method, a crystal of carborundum is partially immersed in molten solder, which, on solidification, holds the crystal tightly, and presumably gives a large area of contact. In the second method the crystal is held by means of three screws in a metal cup filled with mercury. In the third method (figure 1) the crystal is clamped between two pipe-clay tubes, through which pass carbon rods (sharpened H.B. pencil leads) which are pressed on to the crystal by springs. The initial resistance of the arrangement is non-linear, of the order of 100,000 ohms at 4 volts. The carbon-carborundum contacts are broken down by passing a heavy current for a short time (e.g. 7 amperes for 10 seconds). The current was obtained from 110 v. A.C. mains with a series limiting resistance. With 7 amperes passing, the crystal reached about 1200° c., judging from its colour. The specific resistance while at bright yellow heat was measured as 0·07 ohm/cm³ (black carborundum). This rose on cooling to about 5 ohms/cm³ In this experiment it was impossible to tell how much of the resistance was localized at the contacts and how much represented *volume* resistivity.

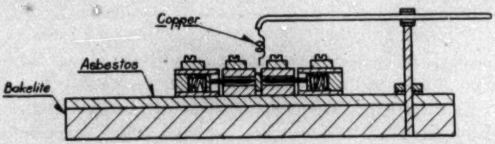

Figure 1.

In figure 2, curve I represents voltage plotted against current for two fused carbon-SiC contacts in series, prepared as above. The resistance is linear, of the order of 100 ohms, up to about 7 volts. In curve II, two solder-SiC contacts are in series. The resistance is linear, of the order of 1 megohm, only up to about 0·5 volt. A similar curve is obtained for mercury-SiC. In curve III, a solder-SiC contact is in series with a cat's-whisker contact of copper wire. The two separate branches of these curves represent the two different directions of applied voltage. Curve II coincides with one branch of curve III, since the direction of easy flow of electrons for the high-resistance (cat's-whisker) contact necessarily corresponds to the direction of difficult flow for the low-resistance (solder) contact. The dotted branch of curve III is obtained when a fused carbon contact is substituted for the solder contact. For this low-resistance branch of curve III, the solder contact is evidently only satisfactory at low voltages, and this condition is most definitely *not* obtained in much of the published experimental work on crystal rectification. The fused carbon contact used in the present work has such an exceedingly low resistance that distortion of the low-resistance branch does not occur.

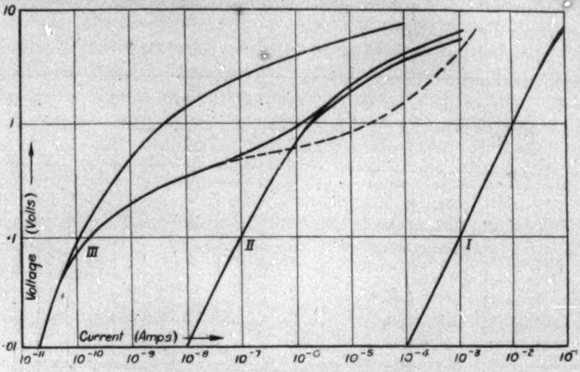

Figure 2. Typical current-voltage relationships.
I. Two fused carbon contacts.
II. Two solder contacts.
III. Cat's whisker and solder contacts.

§ 3. EXPERIMENTAL RESULTS

The electrical circuit is shown in figure 3. *Voltage* is measured by the multi-range voltmeter connected directly across the carborundum crystal and series resistance. The voltage drop across this resistance is allowed for when it is significant. Unfortunately this method of measurement, although simple and direct, gives the voltage across *two* metal-SiC contacts. In practice one makes the resistance of one contact small compared with the resistance of the

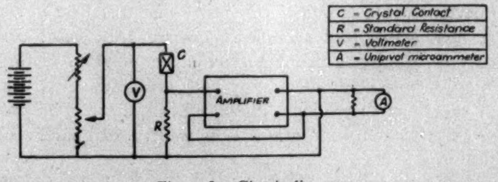

Figure 3. Circuit diagram.

other, as described above. *Current* is measured by measuring the potential drop across the series resistance, which is variable in steps from 10^2 to 10^7 ohms. For this purpose a D.C. amplifier similar to that described by Vance (1936) is used. This has an input impedance large compared with 10^7 ohms, and is connected so as to give 100 % negative feed-back. The voltmeter in the output stage measures 0·1 or 1 volt full-scale, and the current range is therefore 10^{-8} to 10^{-2} amperes for full-scale deflection.

Experimental curves relating current and voltage for single carborundum contacts are shown in figures 4 and 5. It should be clearly understood that while these curves are *exact* for the given contact and conditions, they are only *typical* of the given contact materials. This limitation will be readily appreciated by anyone who has done any experimental work on crystal rectification. For those who have not, it is as well to emphasize that the effect of such factors as contact pressure, actual (not superficial) contact area, exact composition of contact materials, thickness of any surface layer, previous history of contact, etc., which are factors controllable only with great difficulty, can cause great variation of experimental results. These difficulties are often glossed over in accounts of experimental work, and it is as well to read such accounts with a highly critical eye.

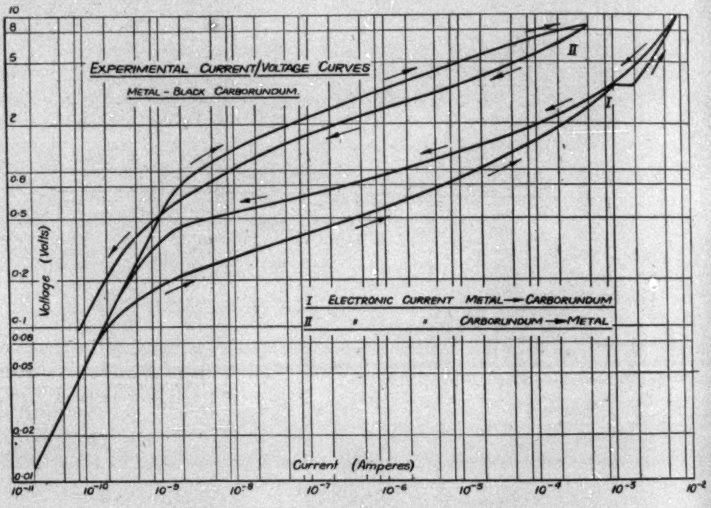

Figure 4.

The contact combinations studied are shown in the table, which gives in each case the number of *different* crystals studied, the number of observations using different parts of the *same* crystal and the overall experimental variation observed. The last is expressed arbitrarily by the range of current for a voltage of 1 volt applied across the contacts. This variation is generally enormous (showing the effect of uncontrolled factors), but this does not invalidate the conclusions given below, for the *direction* of rectification is constant, and for a particular contact the current-voltage curves are approximately repeatable.

In figure 4, a current-voltage curve is given for a cat's-whisker contact of copper-black carborundum. The direction of easy flow of electrons is from metal to semi-conductor. In obtaining this curve, the voltage was raised in small steps to the maximum value and the corresponding currents measured; the voltage was then decreased similarly. This procedure results in two curves for ascending and descending voltage, showing that the current at a given voltage depends on the time of application. A point to notice is that in the direction of easy flow of electrons the current *decreases* with time of application of voltage, while in the direction of difficult flow the current *increases* with time.

Table. Contact combinations studied

Contact	No. of different crystals	No. of different points on same crystal	Total range of current (amp.) at $V=1$ volt	
			Metal +	Metal −
Copper-black SiC	25	10, 10, 6, 2 (remainder 1)	$3\times10^{-9}-6\times10^{-7}$	$4\times10^{-8}-3\times10^{-5}$
Solder-black SiC	4	(all 1)	—	—
Mercury-black SiC	2	1, 1	—	—
Fused C-black SiC	6	(all 1)	—	—
Copper-green SiC	6	3, 2 (remainder 1)	$8\times10^{-6}-1\times10^{-5}$	$6\times10^{-7}-1\times10^{-6}$
Solder-green SiC	1	1	—	—
Mercury-green SiC	1	1	—	—
Fused C-green SiC	1	1	—	—
Green-black SiC	2 pairs	4, 1	$6\times10^{-5}-3\times10^{-4}$	$5\times10^{-8}-8\times10^{-6}$

In figure 5, curve I refers to a cat's-whisker contact of copper-green carborundum. It has been found that the resistance of contacts with green carborundum is always less than similar contacts with black carborundum. Rectification is in the opposite direction, the easy flow of electrons being from semi-conductor to metal. The effect, described in the last paragraph, of the current varying with time was not noticed. Curve II refers to a contact between crystals of green and black carborundum. Rectification is in the direction to be expected by analogy with the results for metal-carborundum contacts, the easy flow of electrons being from green to black carborundum. Contacts of green-green and black-black carborundum also rectify, but less efficiently.

Other experimental points of interest are: similar results were obtained with dull, shiny, striated and fractured surfaces. The crystallographic orientation of the surface was immaterial. Similar results were obtained on a surface which had been exposed to the air for a long time and on newly fractured surfaces.

Heating the crystal in an atmosphere of nitrogen or prolonged washing with hydrofluoric acid had no effect on the contact resistance.

The curves were repeatable except when more than about 12 volts were applied, when the contact resistance began to break down, and was only partially recovered on lowering the applied voltage. At about 20 volts a white glow appeared at the contact. Sillars (1942) has reported that this glow gives a continuous spectrum. Pressure applied to the contact altered the resistance characteristic. With increasing pressure the resistance decreased and became less dependent on voltage.

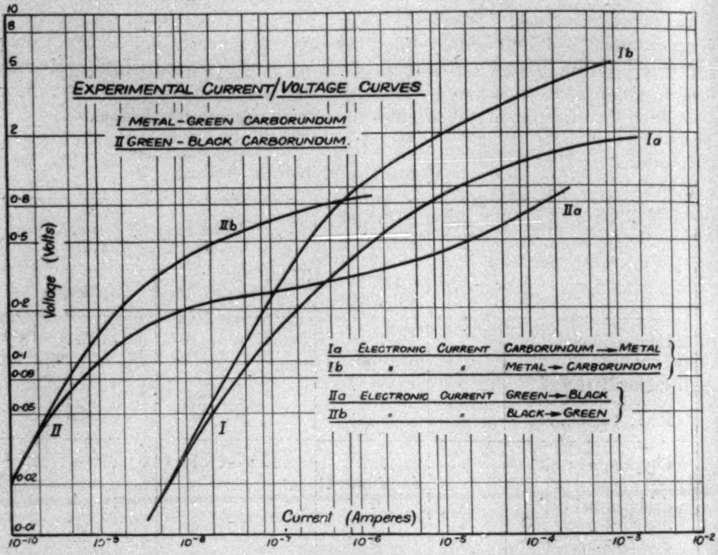

Figure 5.

At low voltages (or, it may be, at low current-densities) the contact resistance is linear. Over a certain voltage range non-linearity is observed, and at high voltages the resistance apparently tends to become linear again. This latter may, however, be a *contact breakdown* effect.

§ 4. THEORETICAL DISCUSSION

It can be deduced theoretically that for an *excess* semi-conductor the thermo-electric force against a metal is *negative*, while for a *defect* semi-conductor it is *positive*. It has been shown experimentally by Gokhberg (1937), and confirmed by the author, that on this count green and black carborundum should be classed respectively as *excess* and *defect* semi-conductors. The cause of this difference is obscure. Carborundum is certainly an " impurity " semi-conductor, but the identity of the impurities is not known.

It has generally been supposed that there is a surface layer of silica on carborundum crystals, acting as a " barrier-layer ", but the evidence is not very convincing. Heine and Scherrer (1940) have, from electron-diffraction experiments, shown that such a layer, if present, must be less than 10 A. thick. Finch and Wilman (1937) have similarly shown that a layer 15 A. thick may sometimes be present, but can be removed by the usual means (e.g. hydrofluoric acid). The fact that a freshly fractured surface is indistinguishable electrically from a natural crystal face shows that any silica film must be formed very rapidly on exposure to the atmosphere. In any case, it is inconceivable that the *thick* barrier-layer (approximately 10^{-3} cm.) required on Mott's theory of contact rectification (1939) can be present. This theory is completely satisfactory only for the copper-oxide rectifier. Wilson's earlier theory (1932) postulates a barrier-layer approximately 10^{-7} cm. thick, and this may possibly be present. Unfortunately, Wilson's theory predicts rectification in the wrong direction. A possible solution to the difficulty may be found in the work of Losev (1940) on the photo-electric effect of carborundum. His experiments indicate that while the bulk of a crystal may have " defect " conductivity, the outer layer (10^{-3} cm. thick) will have " excess " conductivity, the " barrier-layer " occurring at the junction. It does seem necessary to postulate some sort of *physical* barrier-layer, for the formation of an *electrical* barrier seems ruled out by the apparently instantaneous response of the carborundum rectifier to short impulses. One must conclude, then, that the current theories of contact rectification do not apply satisfactorily to carborundum.

§ 5. ACKNOWLEDGMENT

The author wishes to thank Dr. A. P. M. Fleming, C.B.E., Director and Manager, Research and Education Departments, Metropolitan-Vickers Electrical Company, for permission to publish this paper.

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A MACHINE FOR HARMONIC SYNTHESIS

By A. SHILTON,
Technical College, Brighton

MS. received 10 *November* 1943; *demonstrated* 17 *December* 1943

THE addition of harmonic waves is a matter of considerable importance in the theory of sound, of alternating current, and the various branches of telephony, but it has been somewhat difficult to demonstrate this process to students at all adequately without the labour involved in drawing a large number of curves, or the use of elaborate electrical apparatus.

The machine developed by the writer for this purpose is compact and easily portable, and will perform the addition mechanically with considerable accuracy. As shown in figure 1, three similar cylinders have pistons which can be operated by cams, so designed that the motion of the pistons is simple harmonic. The cylinders communicate with each other, and with a fourth cylinder of smaller diameter having a piston which carries the recording pen. The cylinders are filled with oil and the piston of the recording cylinder has a return spring which keeps the oil under slight pressure and thus maintains contact between the other pistons and their respective cams. The recording pen presses on a paper strip wound on a drum, which rotates about an axis parallel to that of the recording cylinder. A single main shaft drives this drum and the cams, maintaining a constant speed relationship between the cams themselves and between the cams and the drum. The cams are driven by interchangeable gears, the drum by a friction drive. Each cam, acting by itself, produces simple harmonic motion of the pen, and this motion, combined with the rotation of the recording drum,

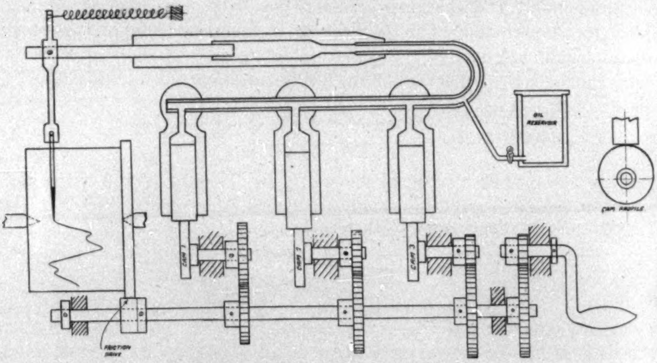
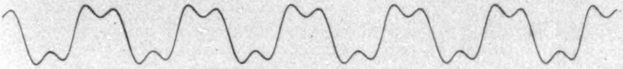


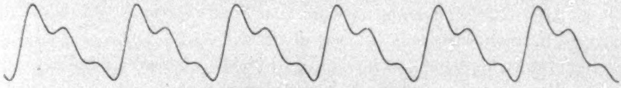
Figure 1. Machine for harmonic synthesis.

makes it draw a sine wave. If more than one cam is put into operation, the pen records the curve resulting from the addition of the component waves which the cams would produce acting separately. These components are under the control of the operator in respect of relative frequency, amplitude and phase.

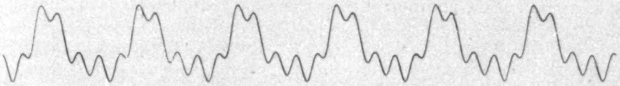
The frequencies depend on the gear ratios chosen to drive the cams, but, in order to preserve the same centre distance, it is necessary that the total number of teeth on each pair of gears shall be a constant. By making this total 60 teeth it is possible to obtain ratios of 1 : 1, 1 : 2, 1 : 3, 1 : 4, 1 : 5, and thus to obtain harmonics up to the 5th.



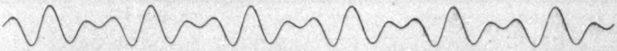
1 FUNDAMENTAL + 3rd HARMONIC



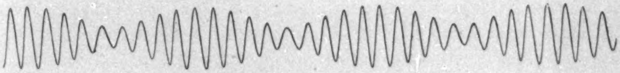
2 FUNDAMENTAL + 2nd AND 3rd HARMONICS



3 FUNDAMENTAL + 2nd AND 5th HARMONICS



5. FREQUENCIES IN RATIO 2 : 3 MUSICAL INTERVAL OF A 'FIFTH'



4 'BEATS' BETWEEN HARMONIC WAVES

Figure 2. Traces obtained with machine.

The amplitudes of the components can be varied by using various cams, which are interchangeable and have different " throws ".

Phase relationships between the components can be adjusted by altering the orientation of the cams with respect to their driving gears. It would be useful, though this was not included in the original machine, to have a scale of degrees engraved on the face of each cam and a vernier arm fixed to the frame of the machine; the setting could then be carried out more easily and accurately.

The main difficulty encountered in the construction of the machine was the necessity of having the pistons an accurate fit in their cylinders. They must, of course, be oil-tight, but must slide quite freely, and this necessitates lapping to an accuracy of about 0·0001 inch. With this degree of accuracy, and using ordinary machine oil, no appreciable leak was observed. The type of pen used is a matter of some importance. In the writer's experience, the most successful was a piece of glass-tube drawn out to a point and ground flat on fine emery cloth. The tube forms a reservoir for the ink, and such a pen is very smooth in action, the recording arm being quite free from any kind of chatter. It is convenient to have a spring-driven drum, on which the paper can be wound after recording.

The machine is suitable for demonstration work on the following topics:—

1. Tone of a musical note—wave-form and harmonic composition.
2. Musical intervals. Frequencies in a simple ratio.
3. " Beats " between frequencies not greatly different. Beat frequency.
4. Modulation of a radio " carrier " wave, and sidebands.
5. Verification of methods of vector addition of waves of the same frequency.
6. Alternating current wave-form. Typical effects of odd-and-even harmonics.
7. Harmonic distortion introduced by valves in audio amplifiers.

Students can watch the curves being drawn, and the manner in which they arise as a result of the addition of their harmonic components is made abundantly clear. It is an obvious advantage to have permanent records for reference, and, in fact, the machine is very useful as a means of obtaining accurately drawn curves which students can use as exercises in the usual methods of harmonic analysis. Examples of traces obtained with the machine are given in figure 2.

THE NON-DESTRUCTIVE TESTING OF METALLIC COMPONENTS

By BRUCE CHALMERS, D.Sc., Ph.D., F.Inst.P.

Lecture delivered 5 *November* 1943

§ 1. INTRODUCTION

The study of metals has in recent years become a recognized sub-division of physics; there are many facets of this subject, the extremes being the application of very difficult physics to properties of metals of purely theoretical interest, and the application of easy physics to pressing practical problems of metallurgy. It is with the latter, less fashionable, subject that this survey deals.

Metals are used in the production of the equipment of modern life on account of a variety of properties, among which mechanical strength and endurance are, perhaps, the most important. Electrical and thermal conductivity, appearance, magnetic properties and a host of other qualities are also important, but only to a secondary degree. The usefulness of a particular piece of metal, which may form part of a locomotive or an aircraft, a fountain pen or a rifle, depends very largely on its mechanical properties, that is to say its resistance to excessive distortion. Its resistance to other destructive agencies, such as corrosion, may also be of prime importance. When such components are being manufactured the question arises as to how tests can be applied to ensure that the article will be able to "stand up to" its work for the required period. This is, in the first instance, a design problem, but even with a satisfactory design it is still necessary to find out whether the product conforms in all respects to the requirements.

When the requirement is that the component shall continue to perform a particular function for a specified period, the only real method of test is to try it under working conditions; but having proved the pudding by eating it, there is nothing left to satisfy the perpetual hunger of the production manager. So the full test of every component is an ideal solution, which, in common with many ideal solutions of elementary physics, only applies when the answer is of none but philosophical value.

It is therefore necessary to test a high proportion by inference, and this may be done in many ways; but an important consideration is the extent to which it is justifiable to take a chance. This depends on the particular application involved and on the economic conditions prevailing. For example, while it might be criminal to permit a one per cent chance of failure of an aircraft component, and it might be merely bad policy to take a similar chance in the corresponding part of a car, it may well be cheaper and better to be prepared to give a free replacement in a vacuum cleaner. So the problem of inspection by inference has to be related to the detailed nature of each example.

In order to decide whether a metallic component is able to do its job without actually trying it, it is of course necessary to make sure that it is dimensionally correct. This can usually be done with any required accuracy by means of methods into which I need not enter here. In some cases, however, it is necessary to destroy the object in order to make a direct measurement of some of its dimensions. Such cases often occur in complicated castings, when cores may have shifted. The more complicated the core, the more likely it is to shift and the more difficult it becomes to detect it by direct measurement. A similar problem may arise when it is desired to assess the effects of corrosion or erosion in tubes, etc., during service after assembly. The second problem is to discover whether it is strong enough, taking the most general meaning of the word, to withstand the stresses to be imposed on it for a sufficiently long time. The third aspect is to determine whether its surface is physically and chemically suitable to its proposed environment.

Two methods of attack are available for these problems: one is to ensure that the article is produced by a process that is known to be similar in all respects to the process that is known by direct test to give a product of satisfactory properties; this may apply to all three aspects previously mentioned, namely, geometrical, mechanical and surface properties; and it is, in fact, used quite widely in the last of these; a surface produced in a given way, e.g. by grinding, honing, etc., can often be assumed to be sufficiently similar to another surface produced in the same way; so also with the chemical condition of the surface, where the detailed process of anodizing, plating, or other finish may define the result sufficiently accurately. For mechanical properties, especially in cases where the factor of safety is not large, it is not usually assumed that a standardized process is a sufficient guarantee of a standardized product. There are good reasons for this scepticism, arising partly from the multiplicity of processes through which any metal article passes from the raw materials to the finished job, and also from the variability of the raw materials themselves. No two casts of steel are ever quite the same, no two ingots are quite identical, and all the subsequent processes depend to some extent, often to a large extent, on the human element to adjust the conditions of working to the condition of the metal. There are, therefore, always some aspects of the complete process that are liable to vary, and it is logical, as experience shows it to be necessary, to test the product as well as to try to control the process. With regard to dimensions, the most favourable case arises when automatic machines are used, or when die-casting is involved. In such examples it is often not necessary to do more than an occasional test to keep a check on proper working.

§2. DIMENSIONAL MEASUREMENTS

When dimensions cannot be measured directly, there are various indirect methods that may be used; the most useful of these are the radiographic and the electrical methods. The radiographic method will be dealt with more particularly in connection with the detection of flaws. The electrical method has several variants, the general principle being the same in all cases, namely, the measurement of an electrical resistance that depends on the thickness of the section under test. When other conditions are constant this can easily be done by means of the method developed by B. M. Thornton, in which four contacts in a row are used. The outermost pair are the current contacts, and the inner pair are used for the potential difference, which may be measured by direct observation of a galvanometer deflection. The method requires calibration on components of known thickness made of the same material as that to be used in practice. The accuracy of this method is, under good conditions, better than 5 %, but difficulties naturally arise when the specific resistance of the material varies owing to composition or metallurgical condition. This presents a more complicated problem, to which an interesting solution has been suggested by A. G. Warren. This consists in determining the variation in current distribution between two points when their separation is altered in the ratio of four to one, the distances being greater and less than the estimated thickness. The current distribution is assessed by measuring the P.D. between two points at the other two corners of a square of which the current contacts form two adjacent corners. Calibration of this method is necessary, the thickness being related to the ratio between the P.D.-current ratios at the two sizes. The accuracy of this method must depend upon homogeneity and isotropy as regards resistivity, but is independent of the absolute resistivity of the material, as it depends on the current distribution and its variation with geometrical factors.

§3. MECHANICAL PROPERTIES

Reverting to the question of mechanical properties, the inspection procedure has the following possibilities;—A certain percentage may be tested to destruction or for the required life in the actual conditions of use. This may only be possible when the design is being tested before it goes into production. Secondly, a test may be devised that is intended to imitate the working stresses and to give the result much more quickly; for example, a fatigue test may show quite rapidly that a component will stand up to the expected stress range for a very long time, or a tensile test may show that a component is not strong enough for its job. That is to say, a destructive test may be applied, but only to a limited number of samples. Thirdly, a destructive test may be carried out on a specially made part of each article. For example, a casting may have an extra section which is put there specially, so that it may be removed and tested to destruction. This involves the assumption that the sample shares the properties of the parts which are going to be subjected to stress in service, and both the procedures involve the assumption that the right property is being tested. Further, a proof test may be applied; in this case conditions are chosen that will not destroy a sound article but will show up defects. The next alternative is to test each article, or a certain proportion, for indications which reveal the presence of causes which would lead to failure. These may be cracks or internal flaws, and we will return to this subject later. Finally, tests may be made on properties which are known by experience to be correlated with the relevant qualities, which can only be directly tested by destruction.

The last two types of test, which may of course be used together, are often classified as non-destructive tests, and I propose now to discuss them in rather more detail.

Non-destructive tests on metals can be classified in the following way:

Tests for flaws.
Tests of physical properties related to mechanical properties.
Tests for surface protection.
Tests for surface profile.

Tests for flaws

Tests for flaws depend upon a variety of physical phenomena, of which the best known are: absorption of x rays or γ rays; formation of magnetic poles on opposite sides of a gap in a magnetic material; deflection of a magnetic field round a gap; electrical resistance; absorption of liquids in cracks (fluorescent or stain); acoustic; damping capacity; specific gravity; elastic modulus.

The choice of a method for a given case must depend on a number of factors. The kinds of flaw can, in the first place, be divided into those that "outcrop" on the surface and those that do not. In many cases it is safe to say that if there are no cracks at the surface there are none anywhere, and in other cases, as, for example, a component that will be subjected to fatigue conditions, cracks at the surface are much more harmful than internal ones. On the other hand there are plenty of examples, such as castings and welds, where internal flaws may exist without any effect being apparent on the surface. Cracks that extend to the surface may be detected visually, and there are various ways of reinforcing the eye in order to increase the sensitivity or the certainty of detection. One such method is *Glo-crack*, in which a fluorescent material is absorbed into cracks aided by a surface active constituent. The article is then examined under ultra-violet light. The procedure is to immerse the article in a bath of the fluorescent liquid for a sufficient time for the object to take up the temperature of the bath, then to transfer it to a second bath which contains an inhibitor which deactivates the fluorescent material with which it comes into contact. Matters are so arranged that the only material left active is that in the cracks. The method is apparently much better for non-ferrous metals than for steel.

In the case of steel the problem is more satisfactorily solved by the *Magnaflux* method, in which the strong magnetic field that originates from the edges of a crack when the crack is transverse to the general direction of the field is revealed by its action on finely divided iron particles. The method has several variants, depending on the size and shape of the article and the type and direction of crack that is suspected. The article may, for example, be magnetized first and then tested either by dipping it into a suspension of iron dust in a suitable medium, or by pouring the so-called "magnetic ink" over it. Alternatively, it may be tested while it is being subjected to the magnetizing influence. This may be either an external magnetic field or a current through it, according to whether the magnetic field is required to be longitudinal or circumferential. The optimum intensity of magnetization and the relative advantages of using A.C. or D.C. for the magnetizing current are matters on which no general rules can be laid down, as they depend on the details involved.

A third aid to visual inspection is obtained by the oil and whitewash method, in which the capillarity of the cracks is again invoked, but instead of a fluorescent liquid, an oil is used. The presence of the oil is revealed by the local discoloration of a coat of whitewash painted on to the surface after the oil has been applied (often at a raised temperature) and then wiped off. The oil may be made to ooze out by warming slightly.

The methods outlined are in general only suitable for cracks that reach the surface, although the D.C. *Magnaflux* method will indicate sub-surface flaws if they are not too deep. Methods of the next group are applicable to flaws not necessarily of the shape suggested by the term "crack", whether they are at or below the surface. The best known and generally most useful of these methods is that of radiography, in which the absorption of x rays or γ rays by a metal is used to reveal local differences in the thickness of metal traversed by the rays. The observation is usually made by means of a photograph in which the contrast and intensity are under much better control than with direct vision of a fluorescent screen. The limitations of this method are the time taken to get a result which is necessarily qualitative, and the minimum dimension of flaw that can be detected by it. A flaw must reduce the section along the path of the beam by at least 2% to be detected, and it must be of such a width that sufficient of its real depth is effective. The method is therefore best suited for internal voids rather than for cracks as such. It forms an essential part of the established technique for inspecting various types of casting and welded joints where mechanical properties are critical, as in boilers. While the radiographic method is widely used, and has been the subject of many papers and several books, the other methods already named for the detection of internal flaws are not nearly as well developed or well known as they might be.

Methods involving the detection of the disturbance of a magnetic field by a void can, of course, only be applied to ferro-magnetic materials. Such methods can be divided into two types, namely, those in which a component of external magnetic field is detected in a position or direction in which it would not occur with a sound specimen, and those in which the efficiency of the sample as the core of a transformer is impaired by the high reluctance resulting from the flaw. The former type is exemplified by the Sperry Rail Flaw Detector, in which a longitudinal current fed by brushes sets up an external magnetic field, variation in the direction and intensity of which are detected by pick-up coils or by special thermionic valves whose output is modified by any deflection of its electrons by a magnetic field. In either case the detector output is amplified and a record is produced. In addition, a paint gun is operated so that the positions of any defects are easily observed. The reluctance method has been used for the detection of faults in wire cables, the cable being passed through primary and secondary coils. The primary coil carries A.C. and the output of the secondary is balanced against either a second coil displaced from the first, so that local differences are shown up, or against a second similar unit on a good sample of cable. A similar method has been used for bars and tubes.

In both these methods it is clear that flaws will only be detected if they have a component transverse to the direction of the current or the field in the sample. This is longitudinal in the former case, but in the latter it involves both the longitudinal magnetization and the circumferential eddy currents, so that transverse or longitudinal flaws may be detected, their effects being, however, in opposite directions.

The eddy-current effect, which tends to dissipate less energy if longitudinal flaws are present, can also be used for non-magnetic materials, particularly for tubes, in which such flaws may be expected in view of the methods by which they are made.

Any flaw that is transverse to a direction in which current can be made to flow can, in principle, be detected from its effect on the resistance, which can often be measured by means of a galvanometer connected to two points between the current input and output contacts. Contact resistance is seldom troublesome unless the resistance of the galvanometer circuit is very low, which would usually render the apparatus unduly sluggish. Limitations to all these methods are introduced by the unavoidable existence of variations between samples of the properties on which the tests depend; variation in dimensions within permissible limits may, for example, have more effect on the measured resistance than flaws of dangerous dimension, or the permeability or resistivity may be so dependent on the composition or on physical condition that it masks the variations in reluctance or resistance that would correspond to flaws that ought to be detected. For these reasons tests must be made, covering a wide range of samples, before the indications of these methods of detection can be used for inspection.

The acoustic methods depend on the propagation of elastic waves through the sample. In the simple hammer test, the presence of flaws alters either the natural frequency or, more often, the quality of the note emitted. This is due to the inefficient transmission of waves at the surfaces of cracks, causing excessive damping of the waves, particularly those of higher frequency. This results in the characteristic "cracked" sound. The practice of tapping railway wheels is an example of this test. The measurement of damping capacity is a more refined and objective way of applying the same principles.

The presence of voids or porosity, but not of cracks, may in suitable cases be revealed by a measurement of the specific gravity, into which I need not enter here, except to remark that the elimination of air bubbles can often be facilitated by the use of a wetting agent when a hydrostatic method is used for the volume determination. The last method on the list is that of measuring the apparent elastic modulus of the material of which the component is made. This may be accomplished by measuring the deflection under a known bending moment. The elastic modulus of a metal is a remarkably constant property of the metal, being almost uninfluenced by impurities or by the physical condition of the material. If the dimensional tolerance is small, the apparent elastic modulus may therefore be a good indication of abnormal conditions, such as cracks.

Physical properties

The next tests are those in which a property is measured which is known to be indicative of a quality that is mechanically important. The most obvious example is the measurement of hardness, which in many cases is in itself of no importance, but is an excellent guide to the tensile strength (providing the material is the same and it is only the physical state that is in question). The hardness may be tested non-destructively, and is often used as an indication that heat-treatment has been correct. This is, of course, an accepted method of testing, and is frequently embodied in specifications, so much so that one rather tends to forget that it is often only an indirect test of the strength of the material. Spectrographic analysis is sometimes used in a similar way to verify the composition when it is known that this has an effect on the mechanical properties within limits that are too small to be readily detected by other methods.

Microscopical examination can occasionally be used non-destructively, but the degree of surface preparation required usually puts this method beyond the realm of non-destructive testing. Usually, also, it is desirable that the test should be rapid and objective, preferably expressed numerically in order that large numbers of tests can be made, assessed and recorded quickly.

X-ray crystallography has not figured very prominently in this field, although it has been used in isolated cases where the crystallographic data which it reveals are important. Here again speed and the more complex forms of the result make this method relatively unsuitable for routine inspection. The possibilities are obviously considerable, and will, I think, be widely exploited in the future.

The possibilities of using other physical properties that may be related to mechanical properties of technical importance will be apparent from what has already been said.

Surface properties: *Protection*

We come now to the question of surfaces. The main problems of surfaces can be considered as wear resistance, corrosion resistance and friction. Wear is governed largely by the hardness of the material concerned, but the hardness that matters is that of the surface layer in the first instance and subsequently of the material that is exposed when this is worn away. Hardness testing either in the ordinary manner (by measuring the indentation caused when a spherical or pyramidal indentor is pressed against the surface by a known force) or by a scratch test in which one measures the width of a scratch made under known conditions, can be regarded as non-destructive if used with discretion. Abrasion or wear is often aggravated by corrosion, which is, of course, one of the biggest causes of wastage and failure of metals in service. The subject of corrosion is too complex to enter into here, and often too controversial for a lecture such as this ; but the chief factors, in addition to the environment, are the chemical, physical and geometrical nature of the surface.

The chemical nature of the surface that is exposed to conditions conducive to corrosion can be any of the following: (*a*) the natural surface of the metal, (*b*) the surface of a protective coating of another metal, (*c*) the surface resulting from some specific chemical reaction such as anodizing, or (*d*) a non-metallic paint or other coating.

In many cases the efficiency of the means chosen to combat corrosion can be measured indirectly without subjecting the surface to corrosive conditions. Such a test would come under the heading of non-destructive tests. From a purely chemical point of view (physical and geometrical factors will be considered later) the purity and homogeneity of the metal or the constitution of the non-metallic surface are the main influences to be considered, and apart from analytical tests on material believed to be similar, the only available method is that of polarimetry, which cannot be regarded as absolutely non-destructive.

The continuity of a protective coating, whether of a metal or a paint, is extremely important, especially in those cases in which protection depends on complete covering. The protection of steel by tin, which is normally cathodic to steel, is a case in which continuity is very important. When steel is protected by zinc or cadmium, to which it is cathodic, it is not quite so important, because the zinc and cadmium corrode preferentially, and may be regarded as sacrificial coatings.

The continuity of a tin coating on steel cannot be measured in a completely non-destructive way. The methods of testing for "porosity", i.e. the number of discontinuities in a given area of the coating, depend on allowing some corrosion to occur and measuring its effect by one of several available methods. At the same time the relationship between the porosity and the thickness of the coating is known to be reasonably consistent for all hot-dipped tinplate that is manufactured commercially at present. A measurement of the coating thickness can therefore be used for arriving at an estimate of the porosity. Two distinct methods have been put forward for the non-destructive testing of the coating thickness of tin or other non-magnetic metals on steel. One is the *magneto-tractive* method, in which the force required to detach a magnet from the surface is measured, and the other is the mutual-inductance method, in which the coating forms two gaps in the core of a transformer, the efficiency of which is measured. Two difficulties arise in applying either of these methods: one, to which solutions have been found, is the lack of consistency of the steel base in respect to magnetic properties. The solution is to make a second measurement in such a way that the sensitivity to steel base properties is increased relatively to the sensitivity to coating thickness. The results of the two measurements are combined to give the thickness of the coating. It may be noted in passing that these methods are equally applicable to the measurement of many other types of coating. The second difficulty is that the thickness of the coating on tinplate is never uniform. It is therefore necessary to take the average of a considerable number of readings in order to attain a useful degree of accuracy. This difficulty is less pronounced when electro-deposits are involved, but it must be remembered that deposits containing nickel or cobalt cannot be regarded as non-magnetic. Nickel coatings on brass or other non-magnetic metals can be measured by similar methods, although the accuracy is limited by the dependence of the magnetic properties on the physical state of the nickel.

Surface properties: *Profile*

With regard to the physical characteristics of a surface in so far as they affect its corrosion-resisting properties, little can be said except that they are usually closely associated with the topographical characteristics. For example, fractured, machined, ground or polished surfaces of the same material would be expected to behave differently under corrosive conditions, not only on account of the specific areas and shapes of the surfaces, but also because the crystalline structure at and near the surfaces would be different. Appearance, or the more refined methods of testing for surface finish, can usually be regarded as taking care of the physical properties concerned.

The shape of the surface of a metal is very important when it is one of a pair of rubbing surfaces, and it may be quite important when it is subjected to corrosive conditions or fatigue stresses. Little trouble is caused when a comparatively gross scale of sizes is involved, but when the scale of the deviations from a mean surface is of an extent or depth that may fairly be described as microscopic, the problems are much more complicated. The methods available for the non-destructive testing of the micro-topography of metallic surfaces can be divided into mechanical and optical. In the mechanical methods a stylus is drawn over the surface under conditions designed to make it follow all the undulations, and its movement is magnified and recorded or converted into a numerical measure of the departure from true flatness. There are two general types of instrument is use. In the electrical type, of which the Abbott is the best known, the movement of the stylus causes corresponding changes in a circuit in much the same way as in a magnetic gramophone pick-up. The output is amplified and may either be measured in terms of the root mean square of the departure from a mean level or it may be recorded photographically from an oscillograph trace. In the Tomlinson instrument, which is of the mechanical type, vertical movement of the stylus (which can only move in this direction) relatively to the rest of the instrument is magnified by a very sensitive lever attached to a thin roller, which forms one of the constraints of the moving part. The end of the lever carries a fine point which traces the record on a smoked glass plate ganged to the table carrying the object under examination.

Either of these methods is quite satisfactory for obtaining a record highly magnified in the vertical direction of the line of intersection of a vertical plane with the surface under examination. They are not completely non-destructive, in so far as it is impossible with most surfaces to avoid some damage, but for almost all purposes the surface is not impaired. An idea of the sensitivity obtainable with a good instrument is given by the fact that the micro-inch is the unit in which results are usually expressed.

The chief difficulty is to know how to express the result so that it represents the quality that is sought. The root mean square and the average deviation from the mean level are the commonest ways of expressing the result, but neither of these, nor any other single parameter, can be regarded as a satisfactory description of the shape of a surface. The appearance to an experienced eye of the trace is probably a much better guide, and the wider use of such instruments in the hands of investigators who are in a position to correlate the surface profile with performance in service will undoubtedly lead to the accumulation of knowledge which will eventually be codified into specifications to which inexperienced inspectors can work.

It is certain that the type of surface designed for various purposes will be found to have different characteristics which will not only have different numerical values associated with them, but will also involve different methods of reducing the trace to its numerical values. Consider for a moment the kinds of surface that are likely to be best for such diverse uses as a brake drum, a bearing surface, a surface that is to be painted, a reflecting surface, a cylinder wall of an I.C. engine and a gauge block.

The optical methods are of three sorts, namely, those in which the specular and non-specular reflecting qualities are measured, the "optical cut" method and the interference-fringe method. The first of these is used mainly to assess the decorative value of a bright metal surface; in its most highly developed form, that due to Guild, the integrated value of the diffuse reflection is measured and compared with the specular reflection.

In the optical cut, or Schmalz, method the image of a straight edge is projected on to the surface in a direction inclined usually at 45° to the normal. The surface is viewed at a similar angle on the other side of the normal. The boundary between the illuminated and dark parts of the surface, being the line of intersection of a plane with the surface, follows the undulations of the surface with a magnification of $\sqrt{2}$ in the vertical direction as compared with that in the horizontal. The magnification supplied by the microscope through which the surface is viewed can, of course, be considerable, and photography is straightforward. From such a record, the numerical value can be assessed in the same way as from the other techniques. The lower limit to the degree of roughness that is susceptible to examination by this method is set by the working distance of the objectives used, bearing in mind the fact that the surface is at 45° to the axis of the optical system. Depth of focus is not a limiting factor, as the whole of the line of demarcation should be in focus at the same time. It is rather the severely practical difficulty of getting a high-powered objective close enough to a surface inclined at 45°.

Another method, developed by Mr. Kayser for the inspection of engineering surfaces, particularly cylindrical ones, consists of the observation of interference fringes formed between the object under examination and a flat plate when monochromatic illumination is used. In a more primitive form, this technique was shown a few years ago at the Society's annual exhibition. The fringes mark the contour lines at intervals of one-half wave-length of the light used and give an indication of the shape of the surface in three dimensions, as opposed to the two dimensions dealt with in the mechanical and optical cut methods.

§4. CONCLUSION

In conclusion I would like to say a few words on the relationship between testing methods and inspection procedures. The problem can be stated as follows: how should a method of test or a combination of methods be applied in order to ensure that a specified performance shall be maintained? This can be split up into several general cases, the first being that in which there is known to be perfect correlation between the quality concerned and a non-destructive test. Here the non-destructive test can be applied to every component, or it may only be possible to use it for testing a proportion. The latter state of affairs need not be regarded as disadvantageous if a proper sampling procedure is adopted and if correct use is made of the results. The principles that should be adopted for using such results have received considerable publicity recently under the name of "quality control". The same remarks apply to the more usual case that arises when the correlation between the non-destructive test and the property concerned is less than 100 %, but is still fairly high.

Another state of affairs occurs when the correlation is still real but is lower, owing to the incidence of factors that are variable only over a long time or between one production unit and another. The correlation would then be good as regards a restricted time period and one unit, but the constant would not be known. In this case the most favourable procedure is to use the non-destructive test on a reasonable proportion to permit the selection of a small sample that is thus known to be characteristic of the batch or to represent a fraction at the worst end. These samples are then subjected to a destructive test.

The application of statistical methods to inspection has another effect which is also very desirable. It points the way to a much closer integration of inspection with production, with the result that production gets an early warning of incipient trouble, often in time to avoid the development of a tendency to the stage at which rejection becomes necessary. Rapid non-destructive tests able to detect departures from consistency of a process can, if correctly applied, be of great use from both the inspection and the production points of view.

I would add that the general nature of most of my remarks is necessitated by the general applicability of the principles involved, non-destructive testing being equally desirable for the hair-spring of a watch, which should have a life approximating to infinity, and for certain products whose useful life may only be a small fraction of a second.

DISCUSSION

Mr. G. L. Bailey. My first duty and pleasure are to offer the sincere thanks of the London Section of the Institute of Metals for your kindness in inviting us to this meeting. The good attendance of the Institute representatives is evidence of their appreciation of this invitation, and I am sure they have not been disappointed.

The Institute of Metals, as you may well know, is very alive to the importance to metallurgy of developments in modern physics, and the Council of the Institute has just appointed a Committee to stimulate and encourage contacts between metallurgists and physicists. It is felt that the metallurgist will derive great benefit from a clearer knowledge of what the physicist is doing, and trying to do, and that, on the other hand, the physicist will also derive great benefit in his work on metals from a clear knowledge of the problems and difficulties with which the metallurgist is faced. I think your Committee was aware of this decision and that your invitation was issued for that reason. The evidence this provides of the willingness of the physicist to co-operate with the metallurgist is of the greatest importance, and I, personally, appreciate it very much indeed.

Dr. Chalmers' lecture dealt with so many interesting points that one cannot mention them all. I should like to say how particularly interested I am in methods of testing protective coatings, particularly determinations of thickness and porosity. I should like to correct, however, a common misapprehension about the value of zinc coatings which something Dr. Chalmers said might encourage. Certainly zinc has great merit in that it is anodic to steel and protects the underlying metal at pores and discontinuities in the coating. This protection is effected by sacrificial corrosion of the zinc. This fact is undoubtedly very important in practice, but is not the whole story. Once a considerable area of the basis steel is exposed, failure of the article is almost certain because anodic corrosion of the zinc to protect that bare spot of steel inevitably leads to the removal of the zinc coating over a wider and wider area and the ultimate corrosion of the steel. Sacrificial corrosion can therefore only give a temporary protection, and the long life of zinc-coated steel in many circumstances is due to the intrinsically good corrosion resistance of zinc.

Mr. H. A. Dell. I wish to add a few remarks in connection with the " transformer " method of testing magnetic materials that has already been mentioned. If this system is operated as a comparator in which a specimen to be tested is compared with a standard, both being placed in similar magnetizing coils fed with alternating current and both surrounded by similar secondary windings, then by connecting the secondaries in opposition and applying the difference signal produced to a valve amplifier the sensitivity of the whole apparatus may be made very high indeed. It is the custom to apply the signal so obtained and a comparable signal representing the magnetizing field to the two pairs of deflecting plates of a cathode-ray tube. A cyclic figure is thus drawn representing the difference between the hysteresis cycles (or rather the first derivatives of the hysteresis cycles) of the two specimens examined. If the conditions are suitably arranged—i.e. maximum magnetizing field, etc.—the shapes of the curves obtained are clearly indicative of the relative nature of the specimens, and changes in the curve are easily visible when, for example, differences of only a few degrees in heat treatment have been made. The usefulness of such a method in mass production is apparent when it is remembered that with small parts up to a thousand pieces an hour may be tested with certainty.

An interesting development of this method is possible when the frequency of the energizing current is varied, for by this means, due to the magnetic " skin effect ", the magnetization is constrained to lie more and more at the surfaces of the specimens as the frequency is increased, so that their magnetic states at different depths may be effectively compared.

Dr. W. Betteridge. Referring to the question of the measurement of thickness of non-magnetic materials by electrical conductivity measurements, the eddy-current induction method is by far the most convenient, since no contacts are required, but it must be remembered that the magnitude of the induced current is controlled by the impedance, and not the resistance, of the current path, and I have found, in the case of relatively thick sections of low-resistivity material, that the inductance of the path can be of more importance han the resistance. The former is usually not related to the thickness of the material, and the sensitivity of the measurements is, therefore, reduced. In such a case it is advantageous to use as low a frequency as possible in order to reduce the importance of the inductance term.

The magnetic testing of steel components is a subject of much interest because of the ease with which two samples can be compared by making them the cores of two identical transformers, the primaries of which are connected in series and the secondaries connected in opposition, so that with identical specimens no e.m.f. results. Any lack of balance detected indicates a difference in the specimens, but, except in a few cases, the nature of the difference cannot be determined. There have been several papers in the last few years dealing with the change of magnetic properties of steels with differing heat treatment, but equally important is the sorting of mixed steels of various compositions, and information is required as to the way in which the magnetic properties of steels in a standard condition of heat treatment, for example normalized, depend on composition, so that reliable methods of identification can be developed.

Mr. T. H. Turner. It is surprising how little we have really learnt regarding the non-destructive testing of large components such as are to be found in marine, railway and heavy electrical engineering. Despite the many pretty, and in their limited fields most effective, tests, such as magnetic, fluorescent, spectroscopic and x-ray, we are thrown back on many time-honoured practical tests for the all-essential maintenance inspections of many irregularly shaped large components.

For example, whitewash is most effective on steam-engine side rods, locomotive wheels and tyres and other such components in which oil will have penetrated any cracks. If struck with a hammer or slightly bent after the whitewash has dried, the oil smear above a crack is unmistakable. If the wheels or other components be " boshed " in caustic solutions and freed from paint and oil, the cracks are actually hidden, and may be shown up once more by oiling and whitewashing.

The answer to the problem the author has set himself is complicated by the fact that what is permissible in large components may be quite impossible in smaller ones. Thus with large components, a trained engineer's best non-destructive test instrument is his own experience-aided eye. He may aid it with lens, sulphur print or deep etching in some cases, and his penknife alone can tell him much about the hardness and brittleness of a surface.

His knowledge of the specific gravities and colours of alloys and their corrosion products is also of the greatest help, as is his knowledge of the type of service stresses and their relation to observed surface phenomena.

The discussion has rather run on the lines of crack detection, and there was much more in the author's subject than that. Some examples may be quoted. It may be recalled that in the early days of the most successful German lighter-than-air trans-Atlantic ships, one limped home with, I think, four of its five Maybach engines *hors de combat* through crank-axle breakages.

In the engineering research, lacquers were used to show the way in which the crank axles deformed below their yield point. Such lacquers cracked as the steel stretched, thus showing where the steel had stretched and, therefore, the location of dangerous stress concentration. These lacquers are very sensitive to temperature variations, and the tests thus required constant-temperature and humidity laboratories. In a crude form, whitewash has been used for the same purpose on bridges.

In workshops, sparking on a grindstone is often used as a quick non-destructive test to show the carbon or other alloy content of steels. X rays have proved disappointing as a means of showing up cracks in steel because the cracks do not run straight, but twist and fork according to crystal orientation and grain boundaries. They seldom or never correspond, therefore, to the straight-line passage of x rays. On the other hand, in less dense materials such as Elektron castings, x rays show up blow-holes and large cracks with the greatest of ease.

Two other practical tests may be worth mentioning. In large turbo-rotors, clinks may be present as lens-shaped transverse cavities invisible from the outside. A relatively small longitudinal hole bored through the centre would cut any such clink. To inspect the inside of such long holes, a microscope which gave one a magnified image of the bore-wall as reflected from a mirror inserted down the bore, and sometimes many feet from the microscopic eyepiece, was developed, and one variety is named the " boroscope ".

This reminds me of guns, and that I was shown in one of the American arsenals, seventeen years ago, and I believe the French had experimented with the process still earlier, the auto-frettage of gun barrels. This replaces the non-destructive proof charge of explosives with a steadily applied but enormous hydraulic pressure of 50,000 tons/sq. inch, surprisingly enough conveyed to the gun in a pipe of only about 1 inch external diameter. This process is applicable to long narrow objects, but not to drum-shaped ones like turbo-rotor retaining rings, owing to the difficulty of retaining the pressure in the end closure.

The ringing of metals with a hammer is used in almost all workshops and can tell much to the skilled engineer. The famous railway wheel-tapper can thus detect a loose steel tyre.

Dr. R. F. HANSTOCK. Dr. Chalmers referred to measurements of damping capacity in relation to non-destructive testing. The technique of measuring the damping capacity of cylindrical bars in torsional vibration at natural resonance frequencies and at very low stresses has been developed considerably by the late Dr. Frommer, and a paper describing his work will be published in due course.

Briefly, when the torsional mode of vibration is employed, damping due to external factors can be reduced to an amount which is small compared with the internal damping of the material ; this intrinsic damping is then found to be sensitive both to the metallurgical condition and the presence of faults in the specimen. Sometimes it is possible to locate the faults by exciting overtones in the bar, since a discontinuity has the greatest influence on the value of the damping capacity when it occurs at a vibration node.

Mr. J. HITCHCOCK. I have not noticed any reference in Dr. Chalmers' address to the widely used method of inspection involving etching of finished components. This, I believe, is a very useful non-destructive inspection tool which is inexpensive to operate. I notice also that Dr. Chalmers has mentioned the vexed question of " cast-on " test pieces ; I think it is now understood that this practice had been discontinued as giving no worth-while information, and where a test piece is required, the standard practice is to cast it separately.

Mr. E. G. STANFORD. Dr. Chalmers has given a general survey of many of the methods for the detection of cracks in metallic components, and in my opinion has conveyed the impression that these methods are quite straightforward and relatively easy to put into operation.

It is the duty of the industrial physicist to acquaint himself with the difficulties confronting the metallurgist and the engineer and to assist by suggesting suitable means whereby problems may best be solved. It is not out of place, therefore, at a meeting such as this, when physicists, metallurgists and engineers are gathered together, to draw attention to some of the difficulties which are associated with crack detection.

The fluorescent method for the detection of surface cracks. This method will undoubtedly become a useful " tool " in the hands of the metallurgist and engineer, but it is not an easy matter to find suitable solutions of fluorescent material which will quickly penetrate small cracks in the wide variety of surfaces which come up for inspection. The condition and nature of the surface has distinct bearing on the success of the method (de Forest, 1943), and the time taken for solutions to penetrate sufficiently into very fine cracks is often of the order of hours, which is a handicap to inspection under production conditions.

The best type of inhibitor and the use of it are by no means established ; further, a certain amount of experience and skill is required to interpret the results observed when the surface is viewed under ultra-violet light.

The detection of cracks in steel rails. The methods mentioned by Dr. Chalmers, using a search-coil device, will undoubtedly detect large cracks of a type which are often so obvious that there is little need for the use of a crack detector at all. For small cracks the method is not very successful ; often the changes in properties of the material of the rail, along its length, have a greater effect on the detecting device than has the presence of a crack.

Resistance tests. In this method contact resistance is a constant source of trouble ; of the two most powerful means of overcoming this, namely, (1) by using a potentiometric method of measurement, (2) by inducing eddy currents into the material and using a detecting system for indicating variations, the latter method can more readily be adapted for rapid examination, particularly in the case of large components.

In all resistance tests, the sensitivity, or ability of a method to detect small cracks, is limited by the heterogeneity of the material under inspection.

Dr. Chalmers did not mention the use of eddy-current methods for the detection of surface cracks. This method involves the use of a hand-search unit, and is quite successful in machined surfaces. Possibilities of the extension of the method to the detection of internal cracks have been described by Gunn (1941).

Supersonic methods. These methods have been mentioned during the discussion, and I should like to emphasize their importance. A considerable amount of research work is being carried out on the use of supersonics, and results so far obtained are most encouraging. Using these methods, it is possible to detect very small discontinuities (e.g. a small hole of 25-thousandths of an inch diameter) situated in a material several inches below the surface.

In conclusion, I should like to stress the fact that the problem of crack detection is a difficult one, and even when a promising laboratory method has been found, the problem of applying it on a production scale is often a more difficult one than the actual laboratory work itself.

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De Forest, T. (1943). "The Fluorescent Penetrant Method of detecting Discontinuities". *Trans. Amer. Soc. Met.* **31,** 3, 739.

Gunn, R. (1941). "An Eddy-current Method of Flaw Detection in Non-magnetic Metals". *J. Appl. Mech.* **8,** A, 22.

Vigness, I., Dingfr, J. E. and Gunn, R. (1942). "Eddy-current Type Flaw Detectors for Non-magnetic Metals". *J. Appl. Phys.* **13,** 377.

Mr. F. C. Johansen. I have delayed my remarks until the end of the discussion in the hope of learning of some notable advance in radiology that would enable the mechanical, especially the fatigue, properties of full-scale engineering components to be predicted before assembly, or periodically assessed during their service life. The value of non-destructive methods of determining the actual state of components incorporated in finished structures is becoming increasingly recognized in view of the uncertainty of inferring the behaviour of full-scale components, often subject to unknown and unreproducible combinations of conditions, from tests on small laboratory specimens. Even full-scale tests, if carried to destruction, are of value only in so far as the behaviour of other machines which the engineer puts into service, and which are his real concern, can legitimately be inferred from them. Service failures suggest that effects, not only of size and shape, but also of metallurgical processes, forging, machining, welding, assembling and erecting, can be important, notably as regards the introduction of residual stresses, the existence of which is often unsuspected and always difficult to detect. Adequate examination of large components in complete machines or structures demands methods of test which are not only harmless, but which are rapid, readily portable, and capable of being successfully used by inspectors with less than highly specialized training. Physicists will do a great service to engineering if they can devise a technique to meet these requirements and, particularly, to indicate inherent original weaknesses or evidence of overstress in components in service, as distinct from (though not, of course, to the exclusion of) methods of detecting flaws or defects that already exist. Many of the non-destructive tests mentioned by Dr. Chalmers in his admirably comprehensive survey and in the subsequent discussion seem hardly applicable to the large, often inaccessible, components of a structure as big as a bridge, a ship or a locomotive. The possibilities of deflection measurements for indicating sources of mechanical weakness have received less attention than they deserve. In this connection reference may be made* to a differential deflection method, developed by the L.M.S. Railway Research Department, for detecting wheel-seat fatigue flaws in railway carriage axles, which is not only completely non-destructive but has the valuable practical advantage of avoiding the necessity for dismantling the component under examination. Incipient axle flaws showing a trace at the surface rarely escape the quite astonishing vigilance of mechanical inspectors in the railway shops, but wheel-seat flaws associated with stress concentration at the press fit commonly occur just within the fit, where they are hidden from sight and can only very rarely be inferred from visible fretting-corrosion debris. The deflection equipment has proved successful to the extent that, during the few months that it has been in use, four relatively small fatigue flaws, each a potential accident, have been discovreed.

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* *Engineering*, 7 Aug. 1942, p. 101 ; *Railway Gazette*, 19 Feb. 1943, p. 190.

AUTHOR'S reply. I should first like to express my thanks to all who have contributed to the discussion ; they have helped to fill in some of the details in what was necessarily a rather sketchy survey of the subject.

In reply to particular points raised, I am grateful to Mr. Bailey for clarifying my remarks about sacrificial corrosion. I was, perhaps unconsciously, comparing zinc with tin, both of which are intrinsically good from the corrosion-resistance point of view. Mr. Dell's remarks on the application of the cathode-ray oscillograph to the testing of magnetic materials are interesting and point to the most promising line for future development as regards speed as well as discrimination. The use of the magnetic skin effect for limiting the region examined to a surface layer of controllable thickness is also promising. Dr. Betteridge will probably be interested in Mr. Dell's remarks on the magnetic testing of components ; the application of the oscillograph gives a good deal more information than a mere measurement of the out-of-balance current. I fully agree that a great deal more information is required on the effect of composition on magnetic properties. The eddy-current method of measuring the thickness of non-magnetic metals has the advantage of not requiring contacts, and it has, in fact, been used continuously on strip or foil as a check on the rolling process. Temperature and composition are the two main variables which must be corrected for or standardized.

I agree with Mr. Turner that the experienced eye, aided by simple tests, can be relied upon in many cases to give a sufficiently accurate answer ; but I think that there can be no doubt that more discriminating tests are needed, especially in the types of structure in which the factor of safety is reduced to a very small value. Further, present conditions make it necessary for much inspection to be carried out by inexperienced operators ; objective tests are desirable in such cases. The " boroscope " is an interesting application of a simple principle, but does not represent a marked departure from the usual practice of optical assistance to the eye.

I am surprised that Mr. Turner should quote such a fantastic figure as 50,000 tons/sq. in. for the auto-frettage of guns. A simple calculation would show that such a pressure, which is far in excess of anything used by Professor Bridgman in his well known work on high pressures, would require an enormous structure to withstand it. A gun would undoubtedly burst before one-thousandth of this pressure had been reached. The purpose of auto-frettage is to improve the mechanized properties of the barrel, and not primarily as a non-destructive test ; it is carried out at a pressure in the region of 25 tons per square inch.

I shall be extremely interested to see the paper, referred to by Dr. Hanstock, describing Frommer's work on the measurement of damping capacity by torsional vibrations at resonance frequency. Mr. Hitchcock mentions the examination of finished components after etching. This, of course, was an omission, and I am grateful to him for pointing it out.

It was certainly not my intention to give the impression, as apparently I did to Mr. Stanford, that all the methods of testing that I referred to are easy to use ; but where the need is sufficient, methods can always be found for applying any useful test, however complicated. Mr. Stanford seems to have been unfortunate in some of the cases in which he has tried to apply methods that have proved successful in other applications ; I would agree, of course, that none of these methods is of universal use, and that the most useful must, in any instance, be selected and tested. I cannot agree that contact resistance is necessarily a source of trouble in resistance measurements, even when no potentiometer is used. The use of eddy currents for detecting surface cracks is, of course, well known. Ultrasonic methods seem to have attracted considerable attention recently, and I think that one may justifiably look forward to useful developments in this field.

I agree with Mr. Johansen that a very large and important problem exists in the examination of large components before and during service. I am afraid that I cannot add anything on this topic to what I have already said. I am very interested in Mr. Johansen's example of the deflection test as applied to wheel-seat fatigue failure.

REVIEW

Tables of Functions with Formulae and Curves, by F. **Jahnke** and E. **Emde**. Pp. 303 + 76 + xvi. (New York: Dover Publications, 1943.) $3.50.

Most physicists probably know the tables of Jahnke and Emde, in which many of us look for those out-of-the-way functions of which we know no other source, like $\int_{-\infty}^{\infty} e^{-y^2z^2-z-xe^{-z}}\,dz$ (a function of x and y).

The collection first appeared in 1909, was much enlarged in 1933, and then re-cast in 1938. On this occasion, the first part, containing tables and formulae relative to the elementary functions, was omitted, and the remainder somewhat further amplified; there was a promise of another volume which would contain the material from the earlier editions on the elementary functions, together with much more of the same nature. This volume has never become available.

The edition now before us is issued by Dover Publications, of New York, under licence of the American Custodian of Alien Property, and contains, in addition to a photographic reproduction of the 1938 edition, an addendum of 76 pages giving the material from the 1933 edition which was omitted in the later one. The opportunity of improving on the original by including a list of errata has been missed.

The sole British agents are Scientific Computing Service, Ltd., of 23 Bedford Square, London W.C. 1, and the English price is 25*s*.

J. H. A.

RECENT REPORTS AND CATALOGUES

Bulletin and Laboratory Notes. (Series 11, no. 12, September 1943.) Pp. 24. Baird and Tatlock (London), Ltd., Halidon, Claremont Lane, Esher, Surrey. 6*d*.

Copper Alloy Resistance Materials. (C.D.A. Publication no. 38.) Pp. 44. The Copper Development Association, 9 Bilton Road, Rugby, Warwickshire.

A list of German publications being reproduced by the Photo-Offset Process under Authorization of the Alien Property Custodian in Washington. Pp. 4. H. K. Lewis and Co., Ltd., 136 Gower Street, London W.C. 1.

Co-ax Articulated Air-spaced Cables for High Frequencies. Pp. 4. Transradio, Ltd., 16 The Highway, Beaconsfield, Bucks.

ERRATUM

Volume 56, *Part* 1, *reverse of frontispiece*

It is regretted that by an error reference was made to " the late Mr. George Watts ". Mr. Watts is, in fact, still alive, and taking an active part in the business of E. A. Watts and Son, Ltd., of which he is Chairman, and at whose factory he is daily to be found.